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da Silva, M.R.C. orcid.org/0000-0002-6073-5688, de Castro Carvalho, I. orcid.org/0000-0002-4588-1011, Silvestro, L. orcid.org/0000-0002-6437-3047 et al. (3 more authors) (2025) *Advances in understanding the mechanisms of particle dispersion and performance of superplasticisers in alkali-activated materials – a systematic literature review*. *Cement and Concrete Composites*. 106360. ISSN: 0958-9465

<https://doi.org/10.1016/j.cemconcomp.2025.106360>

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Advances in Understanding the Mechanisms of Particle Dispersion and Performance of Superplasticisers in Alkali-Activated Materials – a Systematic Literature Review

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Abstract

Chemical admixtures, such as superplasticisers, are urgently needed to support the widespread adoption of low-carbon cements for a net-zero future. This study presents a critical, systematic literature review of 100 publications, focusing on the mechanisms of dispersion, particle-surface interactions, and performance of superplasticisers in alkali-activated materials (AAMs). Key gaps remain in understanding the interactions between metakaolin particles and superplasticisers. Most research centres on alkali-activated slag systems and their interaction with polycarboxylate ethers (PCEs), recommending high-molecular-weight, highly anionic PCEs with short side chains. The high pH and ionic strength of AAM pore solutions, along with shifts in surface particle zeta potential, impair superplasticiser performance due to solubility issues, partial degradation and polymer agglomeration. Future progress will focus on advances in molecular design, the development of novel or modified PCEs, and a deeper understanding of nanoscale and atomic-level interactions. This review outlines existing knowledge and the critical challenges ahead in engineering next-generation admixtures for sustainable cement technologies.

Keywords: Superplasticisers, workability, alkali-activated materials, dispersion mechanisms, particle-surface interactions.

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65 **Acronyms**

66

67 **AA:** Acrylic acid

68 **AAFA:** Alkali-activated fly ash

69 **AAMs:** Alkali-activated materials

70 **AAMK:** Alkali-activated metakaolin

71 **AAS:** Alkali-activated slag

72 **APEG:** α -allyl ω -hydroxy poly(ethylene glycol) ether

73 **CaO:** Calcium oxide

74 **CO₂:** Carbon dioxide

75 **EDL:** Electrical double-layer

76 **EDX:** Energy Dispersive X-ray analysis

77 **EPEG:** Ethylene Glycol Monovinyl Polyoxyethylene Ether

78 **GHG:** Greenhouse gas

79 **HPEG:** α -methallyl poly (ethylene glycol) ether-based polycarboxylate

80 **IPEG:** isoprenyl oxy poly(ethylene glycol)

81 **FA:** Fly ash

82 **FTIR:** Fourier Transform Infrared Spectroscopy

83 **GGBFS:** Ground-granulated blast furnace slag

84 **KOH:** Potassium hydroxide

85 **K₂CO₃:** Potassium carbonate

86 **LS:** Lignosulfonate

87 **M:** Melamine

88 **MK:** Metakaolin

89 **MAA:** Methacrylic acid

90 **MPEG:** Methoxy polyethylene glycol methacrylate-based polycarboxylate

91 **M_w:** Molecular weight

92 **NaOH:** Sodium hydroxide

93 **Na₂CO₃:** Sodium carbonate

94 **Na₂SiO₃:** Sodium silicate

95 **N_{EO}:** Number of ethylene oxides

96 **NP:** Naphthalene

97 **N_{EO}:** Number of ethylene oxides

98 **PAA:** Polyacrylate acid

99 **PC:** Portland cement

100 **PCE:** Polycarboxylate ethers

101 **PEG:** polyethylene glycol

102 **PMMA:** Methyl methacrylate acid
103 **SCMs:** Supplementary cementitious materials
104 **SNF:** Sulfonated Naphthalene Formaldehyde
105 **TEM:** Transmission Electron Microscopy
106 **TPEG:** isopentenyl polyethylene glycol
107 **V:** Vinyl copolymer
108 **VMA:** Viscosity modifier admixture
109 **VPEG:** 4-hydroxy butyl-poly(ethylene glycol) vinyl ether
110 **WRAs:** water-reducing admixtures

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1. Introduction

Alkali-activated materials (AAMs) are one of the existing solutions to reduce the carbon dioxide (CO₂) footprint of the construction sector, as a potential alternative to Portland cement (PC) [1–6]. These materials are produced by chemical reaction (often referred to as alkali-activation) of aluminosilicate materials (precursors) with an alkaline solution (often referred to as the ‘activator’) [7–11] to produce a class of cementitious binder. AAMs have been shown to have associated greenhouse gas (GHG) emissions of 40-80% lower than Portland cement; the extent of GHG emissions achievable depends on the type and origin of precursors used, type, origin and concentration of activating solutions used, water/ binder ratio, etc. [12–15]

Despite the environmental advantages, AAMs face challenges in terms of workability and broader engineering applications [16]. The alkaline activator solutions often produce mixes with high viscosity and limited flowability compared to concrete mixes made with PC [7,17], which restricts the ease of casting, pumping, and finishing in real construction settings. Additionally, variability of mixing design, chemistry of precursors and activator solutions, makes it difficult to achieve consistent fresh and hardened properties in conventional concrete production processes. These challenges limit the widespread applications of AAMs but open the possibilities for developing materials to improve their performance.

Considering the current construction sector, modern concrete mixes often rely on the use of chemical admixtures. They are substances added to concrete to improve one or more properties in both the fresh and hardened states, and are often used in large-scale construction applications where control of these properties is desirable. Many types of chemical admixtures exist, including water-reducing admixtures (plasticisers or superplasticisers), set-controlling admixtures (accelerators or retarders, air-entraining admixtures, shrinkage-reducing agents, and viscosity-modifying admixtures, among others [18,19]. Water-reducing admixtures (WRAs) were introduced in 1930 as a strategy to enhance concrete workability and flow characteristics via particle dispersion, while reducing the amount of water required [20]. The most recent generation of WRAs, superplasticisers, are the most commonly applied admixtures in concrete mixes. They are designed to improve workability and fresh properties while reducing water demand, resulting in reduced porosity and increased strength in the hardened concrete [20,21]. They also enable long-distance transportation, pumping and placement of fresh concrete in reinforced structures [22,23]. The effectiveness of these admixtures is due to

the polymers adsorbing onto the cement particles and facilitating particle dispersion via electrostatic repulsion and/or steric hindrance [24–26].

AAMs typically require the inclusion of superplasticisers with copolymer dispersants to improve their workability and flow characteristics, due to the viscous alkaline solutions used to facilitate the reaction [27]. However, the performance of commercial dispersants in AAMs can differ significantly from their behaviour in PC mixtures, primarily due to the different aqueous and solid-state chemistries of the two systems. For example, AAM activators create higher pH environments and distinct electrolyte conditions [28], while the type of precursor used can alter surface characteristics, such as surface charge, ion content, and morphology. As a result, the interactions between superplasticisers and AAMs are complex, necessitating a deeper understanding of the underlying chemistry to optimise performance.

The main classes of superplasticisers are based on lignosulfonate (LS), naphthalene (NP), and polycarboxylates (PCE) polymers. LS consists of randomly branched polyelectrolyte macromolecules in a lignin structure [29]. They are mainly composed of sulfonate groups, but many other functional groups can be found, such as carboxylic acid, sulfonic acid, phenolic hydroxyl, methoxyl, or a combination of these [30]. The resulting cross-linked structure has a molecular weight ranging from 100g/mol to 400,000 g/mol [31]. Sodium naphthalene sulfonate formaldehyde (SNF, PNS, or NP) is a dispersant commercialised in liquid or powder form as sodium or calcium salts [32]. They have a lower molecular weight (around 1000 to 20,000 g/mol), reaching a higher dispersion after 5 repeating molecules [32,33]. PCE polymers are synthetic macromolecules characterised by a backbone part composed of carboxylate groups, with pendant side chains extending from the main chain, giving a “comb-like” structure. The working mechanisms promoting particle dispersion are predominantly electrostatic repulsion for LS- and NP-based superplasticisers, while the PCE side chains promote dispersion via steric hindrance. Commercial superplasticisers can comprise a mixture of one or more polymers and the addition of various agents, such as defoamer agents, to mitigate the adverse effects of any incorporated air.

Following the success of superplasticisers for PC-based systems, considerable efforts have been made to incorporate these admixtures in AAMs, including LS- [34], NP- [35], melamine (ML)- [36], and PCE- [37] based superplasticisers, among others. However, when these superplasticisers are added to the mixes, they have reduced performance due to several factors: the distinct ionic environment of AAM pore solution, competitive adsorption between

dissolved ions, superplasticisers and particle surface sites, as well as degradation and solubility issues. Consequently, the behaviour of these superplasticisers in AAMs remains inconsistent.

The reasons for this inconsistent behaviour remain unclear, partly due to the lack of detailed information regarding the formulation of commercial admixtures, and their performance is dependent on the choice of precursor or activator and dosage parameters. For example, previous studies have shown that PCEs improve the workability of alkali-activated Class C fly ash and alkali-activated slag (AAS) systems [38,39], with the precursor's calcium content playing a key role in enhancing PCE effectiveness. Conversely, PCEs are less effective in increasing the workability of AAMs based on metakaolin (AAMK) [40,41]. Also, the performance of commercial superplasticisers varies amongst different materials and cement formulations, requiring customised superplasticisers for the desired performance. These facts highlight a few challenges when conducting research on chemical admixtures for cementitious materials, and they show the need for a deep understanding of the role of superplasticisers in AAM systems.

Novel alkali-resistant, high-performance dispersants are urgently needed to enhance the flow characteristics and workability of alkali-activated cements. Regardless of the synthesis parameters, precursor characteristics, or the type of superplasticisers used, a more comprehensive understanding of the underlying mechanisms governing the interactions between these materials is essential. This study applies a critical, systematic review methodology to address this knowledge gap, mapping key research on superplasticisers in AAMs. The primary objective is to identify key remaining knowledge gaps based on the recent advances in understanding the mechanisms of particle dispersion and performance of superplasticisers in alkali-activated materials. The relevant studies, key authors, and influential publications focus on the types of precursors and activation methods employed, particularly emphasising the role and characteristics of these chemical admixtures. Furthermore, this review highlights the interactions and performance of superplasticisers in AAMs based on ground-granulated blast furnace slag (GGBFS), fly ash (FA), and metakaolin (MK), widely used precursors. The findings of this review offer valuable insights into the surface interaction mechanisms amongst different supplementary cementitious materials (SCMs), providing essential knowledge to guide the design of novel, high-performance chemical admixtures for the next generation of AAMs.

2. Research Methodology

A systematic literature review was conducted to ensure the inclusion of the most pertinent studies on the use of superplasticisers in AAMs. The steps of this process are outlined in Fig. 1. This search yielded 366 articles in Scopus. These studies' relevance to the review's scope was then assessed based on access, title, and keywords. Articles that could not be accessed or downloaded, non-compliant studies published in languages other than English, and off-topic papers were excluded. This process reduced the sample to 188 articles. Subsequently, the abstracts of the remaining papers were reviewed, identifying those that did not align with the review's objectives. As a result, a final selection of 100 articles was made for inclusion in this study.

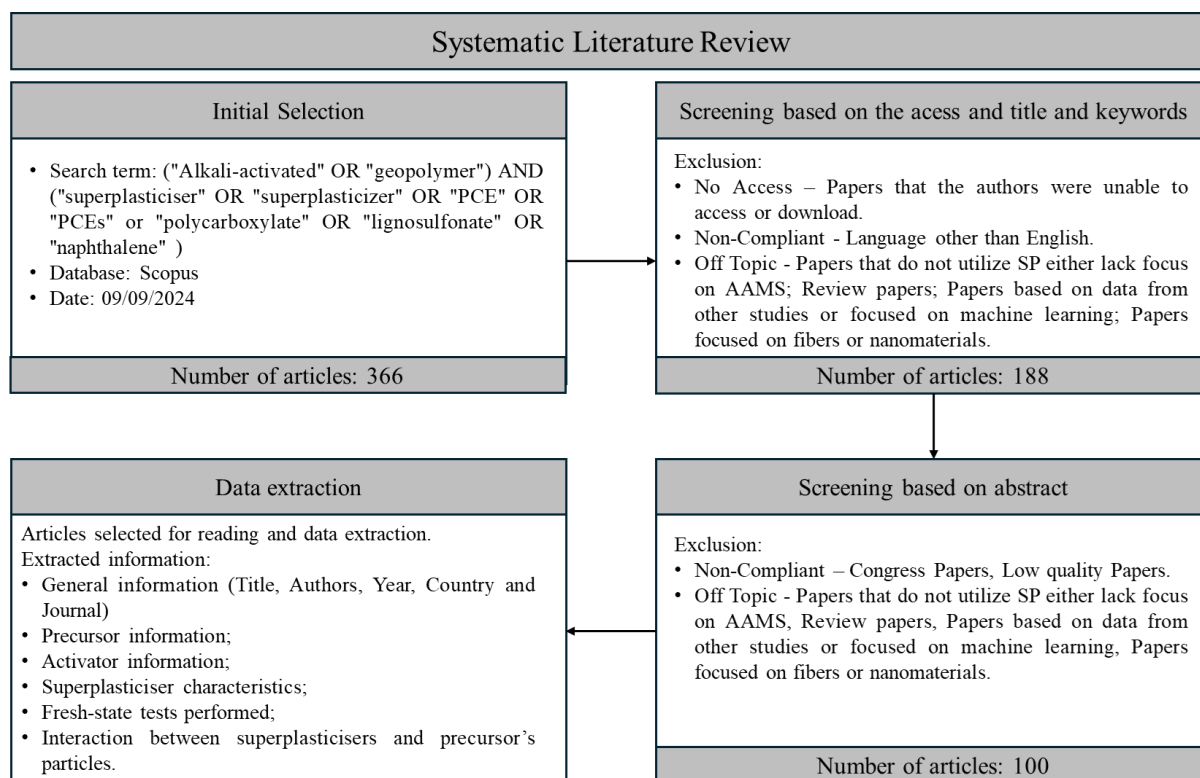


Fig. 1. Steps of the systematic literature review and the criteria applied for excluding non-compliant and off-topic articles, based on access, language, and relevance to the study topic.

To obtain a comprehensive overview of the studies included in the systematic literature review (100 articles), the data were analysed using VOSViewer software. A keyword density map was generated, considering at least one occurrence, as illustrated in Fig. 2. Based on the selection criteria employed in the systematic literature review, a prominence of terms related to 'workability' is observed, as well as the occurrence of key terms for this assessment, such as dispersion, adsorption, and rheology. The analysis also revealed a significant prevalence of terms such as 'compressive strength' and 'mechanical properties', underscoring a predominant research focus on the hardened state of materials. Moreover, studies focusing on fly ash and slag-based systems are more prevalent, highlighting potential research opportunities with materials such as "calcined clays" and "metakaolin", especially considering the wide availability of such precursors globally [42]. Additionally, frontier topics related to the study theme are observed, with particular emphasis on '3D printing' and 'engineered geopolymer composites,' further underscoring the research potential and contributions in these areas.

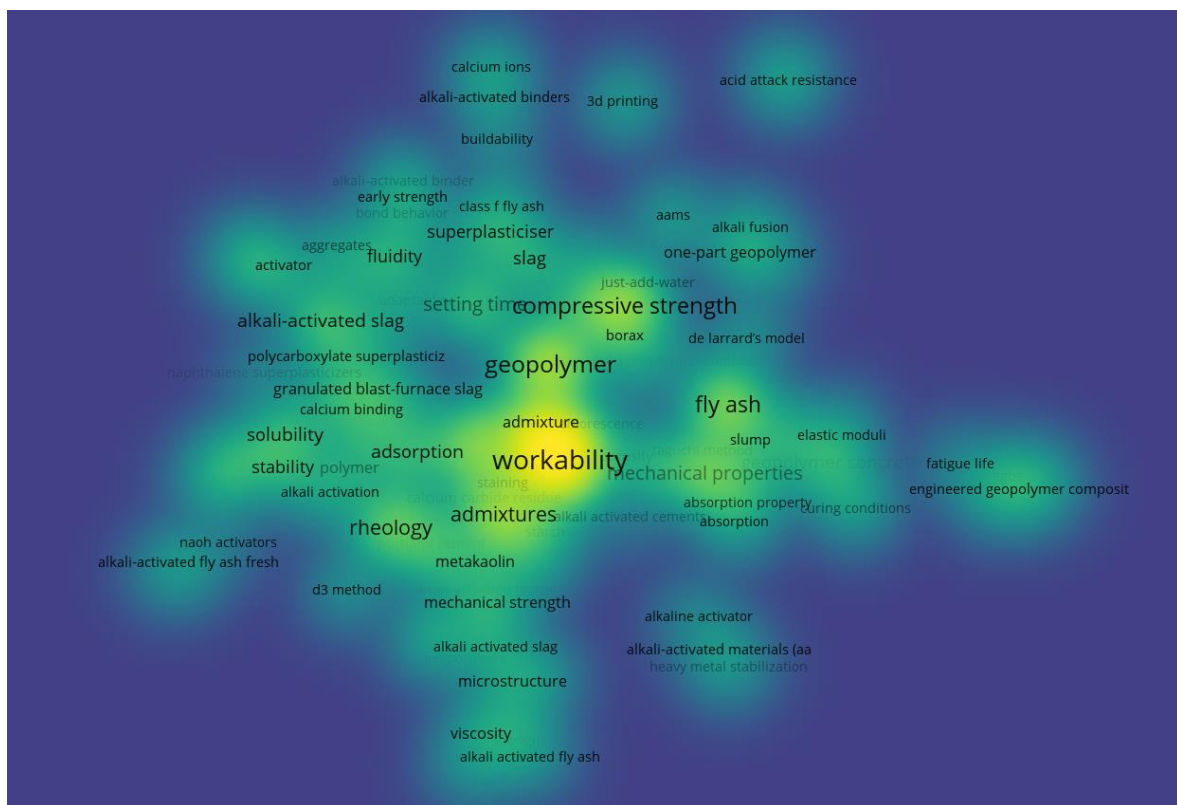


Fig. 2. Keyword density map from the studies included in the systematic literature review on additives in AAMs.

2.1. Bibliometric data of research on superplasticisers for AAMs

2.1.1. Year of publication and geographical distribution

In light of the findings from the research methodology, 100 selected articles were analysed through various bibliometric metrics to elucidate the current landscape of scientific production on the topic. The articles were categorised by year of publication and geographical perspective, considering the first author's affiliation country, to identify nations producing significant advancements in the study of superplasticisers in AAMs. Fig. 3 illustrates the distribution of publication years for the selected papers, indicating an upward trend in the number of publications in recent years, with 17, 20 and 14 articles published in peer-reviewed journals in 2022, 2023 and 2024 respectively. This increasing trend underscores the topic's novelty and highlights the significance of a review paper to advance the field further. Additionally, it is important to note that the study of superplasticisers in AAMs remains largely confined to a limited number of research groups worldwide.

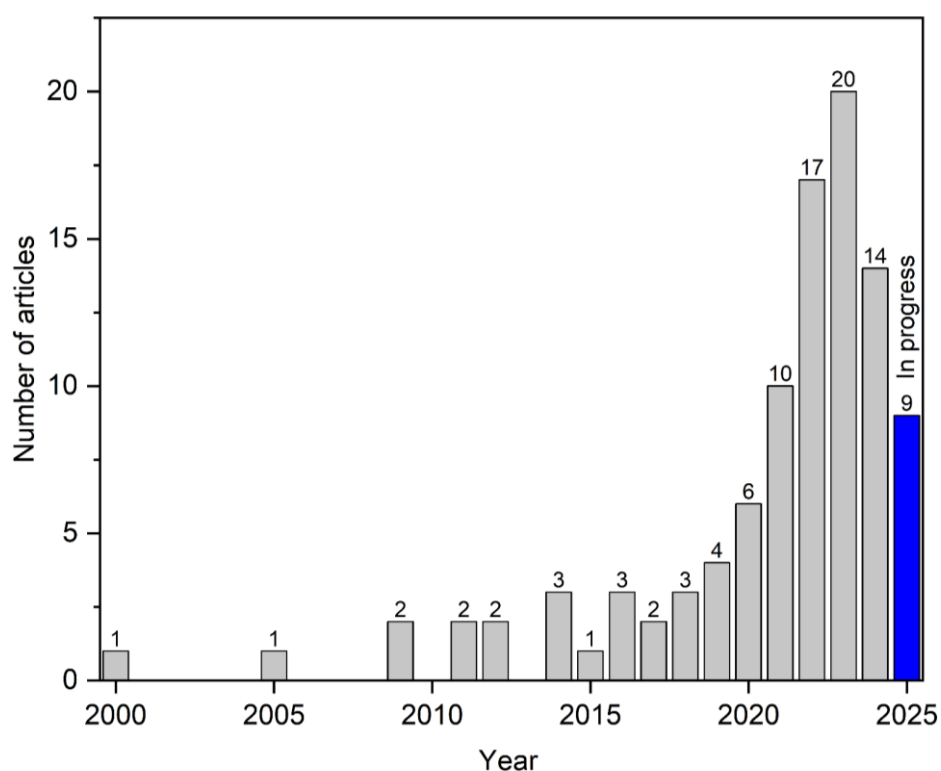


Fig. 3. Number of articles published since 2000 addressing the study of superplasticisers in alkali-activated materials.

The results indicate that China is the leading contributor, accounting for 36% of the total published papers. Additionally, countries such as India (11%), Germany (9%), Australia (8%), and Spain (5%) have demonstrated notable, albeit limited, engagement with this research area. To visually represent these data, a publication distribution map (Fig. 4) was created using a colour scale to illustrate the countries actively engaging in such research.

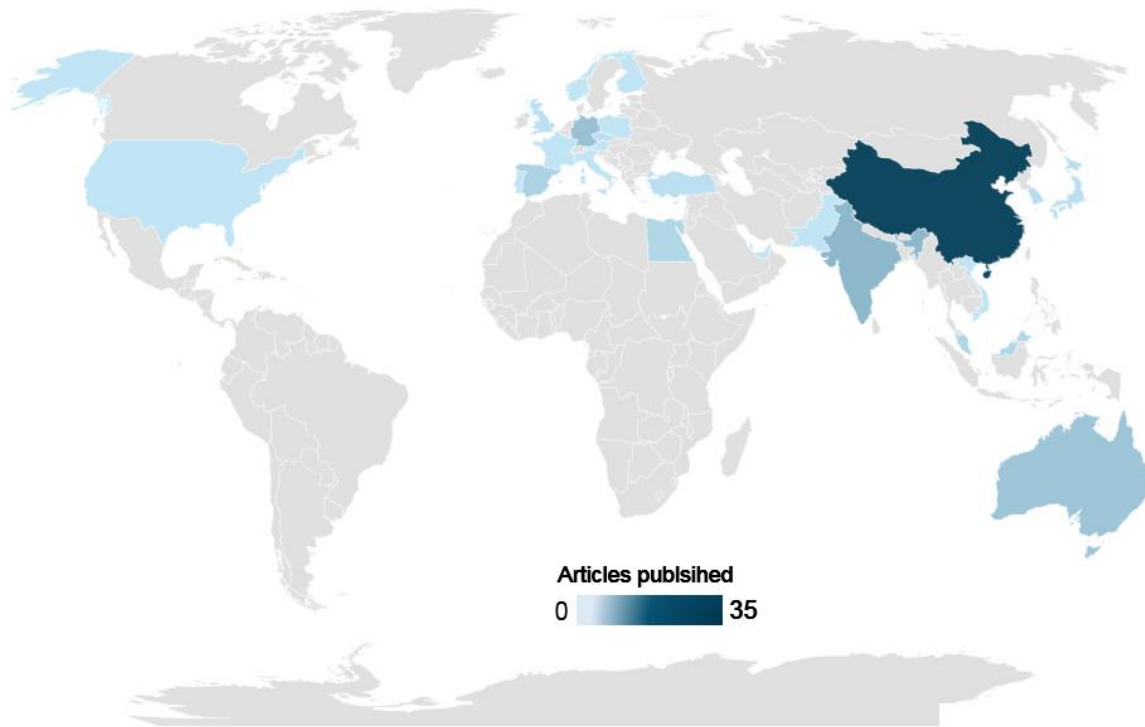


Fig. 4. Geographical distribution of the selected articles.

The geographical analysis encompassed 24 countries, with the majority (17 out of 24) publishing fewer than four articles on the subject. This underscores a lack of significant contributions necessary to advance the study of superplasticisers in AAMs worldwide. In contrast to the substantial body of work on AAMs and the established importance of superplasticisers in PC-based systems, these findings highlight a considerable research gap warranting further investigation.

2.1.2. Mix design and production parameters

Another bibliometric analysis was conducted to summarise key data related to the mix design and production of AAMs. This analysis focused on the types of precursors used, the activators employed, and the sample types investigated (i.e., solution, paste, mortar, concrete, and engineered geopolymer composites). Such an examination is crucial for identifying the current state of the art regarding the use of superplasticisers in AAMs, thereby highlighting existing gaps and established systems within this research area. Regarding the precursors employed, Fig. 5 summarises the frequency of each precursor used in the production of AAMs. It is important to note that some studies utilised more than one precursor in sample production, leading to 142 instances of precursor usage across 18 different types.

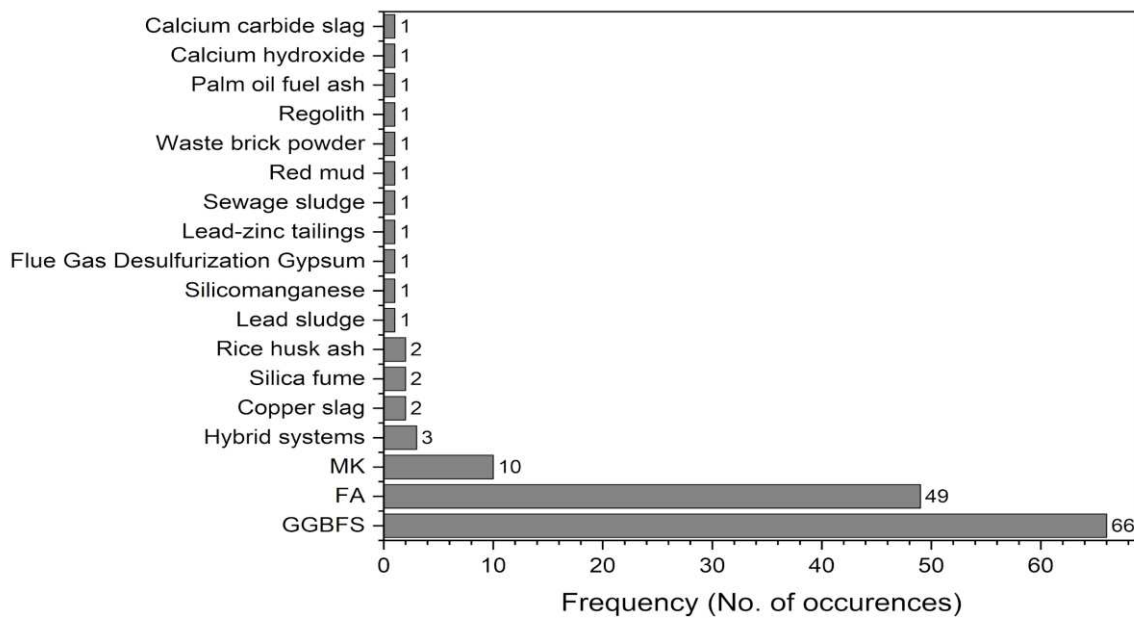


Fig. 5. Frequency of use of different precursors within the selected articles.

The figure illustrates the significant focus on superplasticisers in alkali-activated systems using GGBFS and/or FA as precursors. GGBFS accounts for 46.4% of precursor usage in the selected articles, while fly ash represents 34.5%. This data underscores the dominance of these precursors in the field, indicating that knowledge of systems employing GGBFS and FA is considerably more advanced than that of those using other precursors. Notably, 25 articles reported the combined use of these materials in binary alkali-activated systems. 3 articles reported the use of hybrid systems, where small amounts of PC are used alongside other SCMs and activators.

This analysis yielded important insights regarding the limited investigation of superplasticisers in MK-based systems. MK, produced through the calcination of kaolinite clays, is regarded as a promising aluminosilicate source for alkali-activated systems [4]. The widespread availability of raw materials [43] and the strong performance of MK-based alkali-activated materials [44] position MK as a key precursor for the future, particularly in light of the declining availability of GGBFS and FA, as highlighted by Karen Scrivener [42,45]. Thus, this lower usage of MK, representing only 7.0% of the total precursors' appearance, is important data considering future perspectives of alkali-activated materials research and the increasing importance of this precursor in the academic scenario. Additionally, MK particles are known for their extremely high specific surface area, which results in substantial water demand. This presents key challenges related to rheological behaviour and workability in MK-based systems [41,46]. Given these considerations, further investigations into superplasticiser utilisation in MK-based AAMs are relevant, and the exposed bibliometric analysis identified this research gap.

The selected papers also examined alternative precursors, such as rice husk ash, copper slag, red mud, and waste brick powder. However, current research primarily focuses on understanding and optimising the use of superplasticisers in established and traditional alkali-activated systems. A clear trend emerged regarding the types of activators used (see Fig. 6). Sodium-based activators were the most prevalent alkaline solutions in the selected articles. Specifically, sodium hydroxide (NaOH) accounted for 68 out of 143 activator instances (47.5%), while sodium silicate (Na_2SiO_3) was used in 52 instances (36.4%). Although sodium carbonate, potassium hydroxide, and potassium silicate are also recognised as important activators, their usage in articles focusing on superplasticisers in alkali-activated materials systems was limited, appearing in only 5.6%, 3.5%, and 2.8% of activator instances, respectively. In total, 11 different activators were identified across the 100 selected papers.

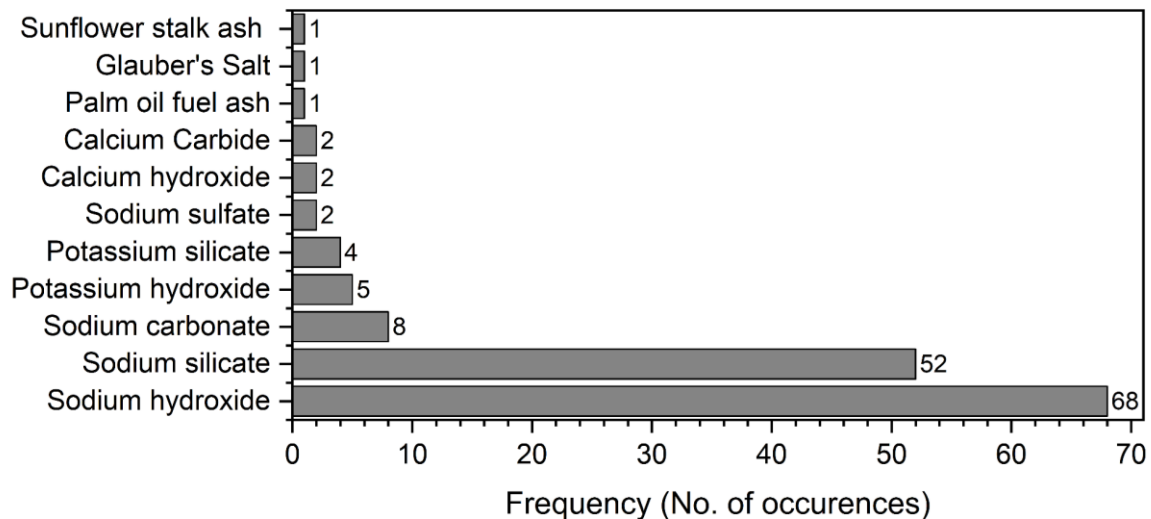


Fig. 6. Frequency of use of different activators within the selected articles.

Considering the types of samples analysed, the majority of papers focused on the effects of superplasticisers in AAMs testing paste-based samples, accounting for 54.7% of occurrences. Following this analysis, 21.7% occurrences of analysis in mortars were found, followed by 11.3% occurrences testing concrete samples, and 10.4% of analysis in solutions among the 100 selected papers. It is important to highlight that the studies involving solutions specifically examined the micro-mechanisms of adsorption between superplasticiser molecules and precursor particles. Additionally, one article reported on an engineered geopolymer composite that did not fall into any of the previously mentioned categories.

2.1.3. Types and characteristics of superplasticisers in AAMs

Fig. 7 shows the occurrence of different types of superplasticisers in the 100 selected articles. Note that the classification was made regarding the main component in the superplasticisers, as commercial superplasticisers usually consist of a mix of multiple compounds. As observed, the ongoing research is mainly focused on PCE-based superplasticisers (72 occurrences), followed by NP- (45 occurrences), M- (24), and LS-based (15) superplasticisers. Recently, rice-husk-based, urea, and starch, amongst other alternative superplasticisers, have been used, opening a new perspective on novel materials to improve the fluidity and/or retention of AAMs.

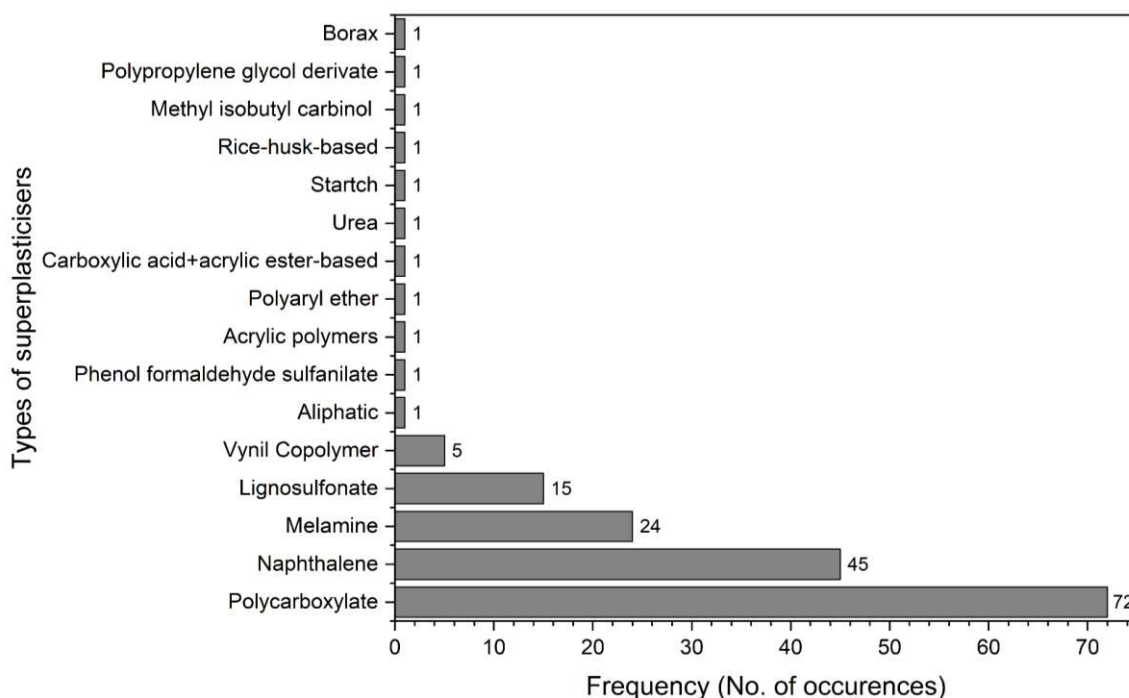


Fig. 7. Frequency of use of different superplasticisers within the selected articles.

Only a few articles provided information on the superplasticisers' characteristics, such as polymer molecular weight (M_w) or backbone/side chain (case of PCEs) molar ratios. This study classified M_w into 3 groups: low (<10,000 Daltons, Da), Medium (10,000-30,000 Da) or High (>30,000 Da). The occurrence of superplasticisers with low, medium or high M_w was 7, 12, and 13 times, respectively, as shown in Fig. 8.

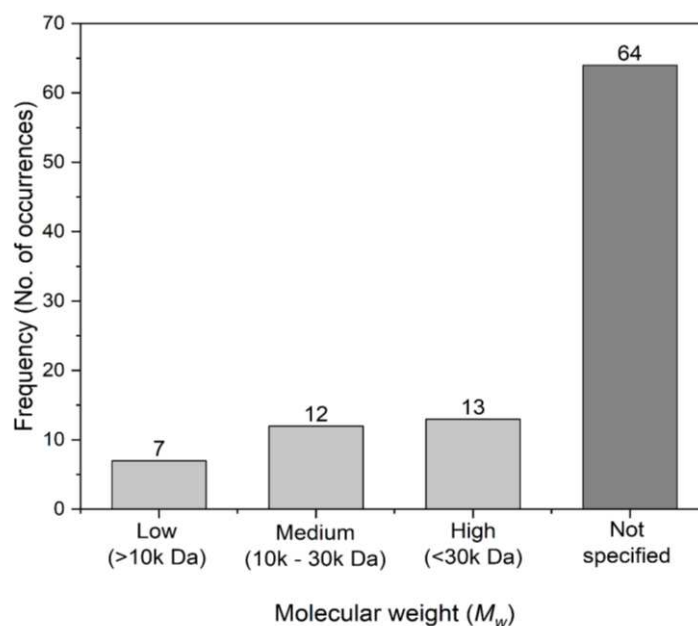


Fig. 8. Polymer's molecular weight values reported within the selected papers.

Fig. 9(a) shows that amongst 72 articles that used PCE, only 18 provided information about the polymer characteristics such as the type of macromonomer and side chain length. The macromonomers identified were APEG (α -allyl ω -hydroxy poly(ethylene glycol) ether), EPEG (Ethylene Glycol Monovinyl Polyoxyethylene Ether), HPEG (α -methallyl poly(ethylene glycol) ether), IPEG (isoprenyl oxy poly(ethylene glycol)), MPEG (Methoxy polyethylene glycol methacrylate), TPEG (isopentenyl polyethylene glycol), VPEG (4-hydroxy butyl-poly(ethylene glycol) vinyl ether)). APEG, MPEG, and HPEG occurred 5 times in the articles (Fig. 9a). In the case of TPEG and phosphate-based macromonomers, 2 occurrences were observed. Also, the use of EPEG macromonomer was reported only 1 time in the papers.

Regarding the side chain (see Fig. 9b), this study classified the PCEs' side chain length into 3 groups: short side chain (<10 Number of Ethylene Oxides, n_{EO}), medium ($10-30$ n_{EO}), and high side chain (>30 n_{EO}). The values of anionicity (molar ratio of backbone monomer to macromonomer) tested were 2, 3, 4.5, 6, 7, 10 and 15. The data suggest a lack of information about the PCEs' molecular architecture, which is likely due to the little clarity from either the supplier of chemical admixtures or a limited description of PCEs' synthesis in the literature. These gaps hinder a deeper understanding of admixture effects, as well as the comparability of results and the reproducibility of studies.

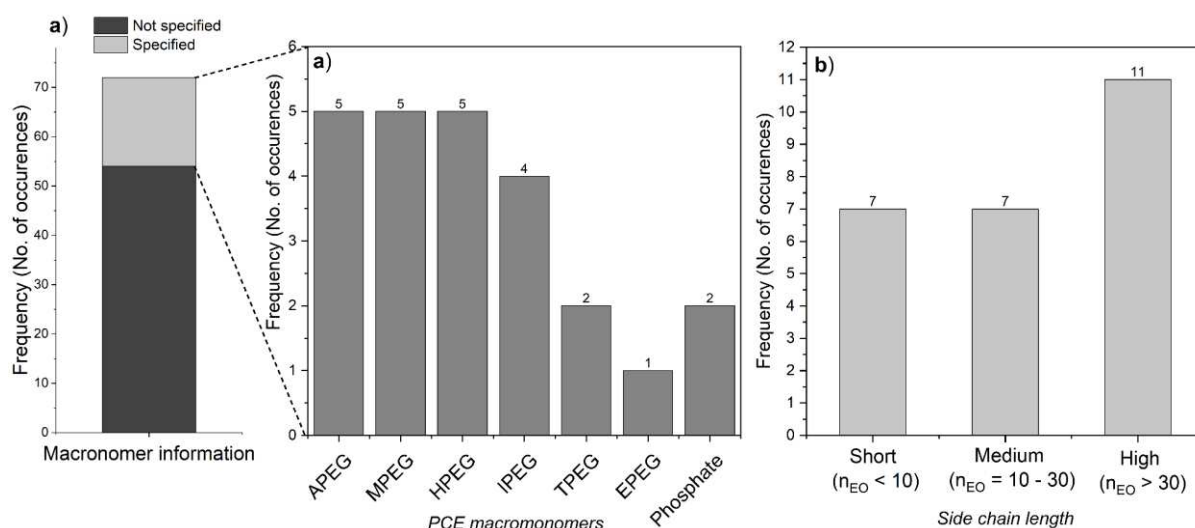


Fig. 9. Molecular architecture characterisation of reported PCE superplasticisers.

2.1.4. Assessment of the flow characteristics of AAMs with superplasticisers

In Fig. 10, the frequency of occurrence of tests conducted on the fresh state of AAMs included in the 100 studies from the systematic literature review is presented. It is observed that expedited tests, such as the mini-slump (54 occurrences), mortar flow test (24 occurrences), and concrete slump test (9 occurrences), are predominant, depending on the type of matrix produced, i.e., paste, mortar, or concrete. These tests are practical and rapid methods for assessing the fluidity of cementitious matrices, although they are considered single-point measurements and are influenced by factors such as the operator, environmental conditions, among others.

In this regard, rheometry tests (rotational or oscillatory) provide a more precise and in-depth rheological characterisation of AAMs, standing out as important tests for evaluating the fresh state and, primarily, the interaction between precursors and chemical admixtures, being characterised by the sensitivity required for this type of analysis, although not extensively applied in studies on the topic with a total of only 29 occurrences. Furthermore, it is important to consider that rheometry tests allow the evaluation of AAMs at different shear rates, enabling the assessment of the material's behaviour for various practical applications, covering a wide range of uses, such as self-compacting materials or those developed for 3D printing, for example.

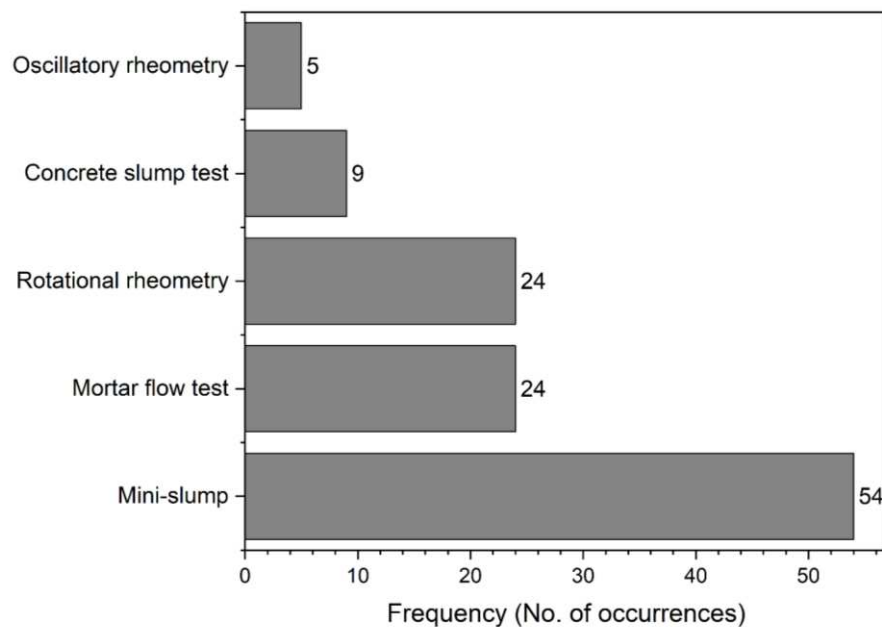


Fig. 10. Frequency of tests conducted to evaluate the fresh-state properties of AAMs.

411 Considering the significance of rheometry tests in the characterisation of the fresh state and the
412 growing interest in research in this field in recent years, particularly for AAMs, Fig. 11 provides
413 a summary of the frequency of studies included in the systematic review, categorised by the
414 type of equipment (Fig. 11a), rotor geometry (Fig. 11b), and the rheological model used (Fig.
415 11c) to determine rheological parameters (e.g., yield stress and viscosity). This information is
416 crucial for advancing the understanding and characterisation of the fresh state of AAMs and
417 warrants attention, as it can influence the results obtained [47].

418 Fig. 11a shows that rheometry is poorly underexplored in the related literature. While
419 rheometers are predominantly used, some studies have reported data obtained using
420 viscometers, which are generally less accurate and sensitive, and have lower torque capacity
421 compared to rheometers. Fig. 11b, shows a lack of clarity in the reporting of testing procedures
422 and configurations. 8 studies did not specify the geometry employed, and have limited
423 information regarding shear rate protocol, gap between plates (in parallel plate geometry),
424 software settings, etc, which significantly impact the results and limit reproducibility.
425 Additionally, Vane and Cylinder geometries are most commonly used, with only two studies
426 employing parallel plate geometries. Unlike Portland cement matrices, AAMs are typically
427 characterised by high viscosity and low yield stress [41]. Consequently, using parallel plate
428 geometry may pose a challenge when placing the material for analysis, as the low yield stress
429 may cause the material to flow on the sample holder, compromising the integrity of the sample
430 analysis.

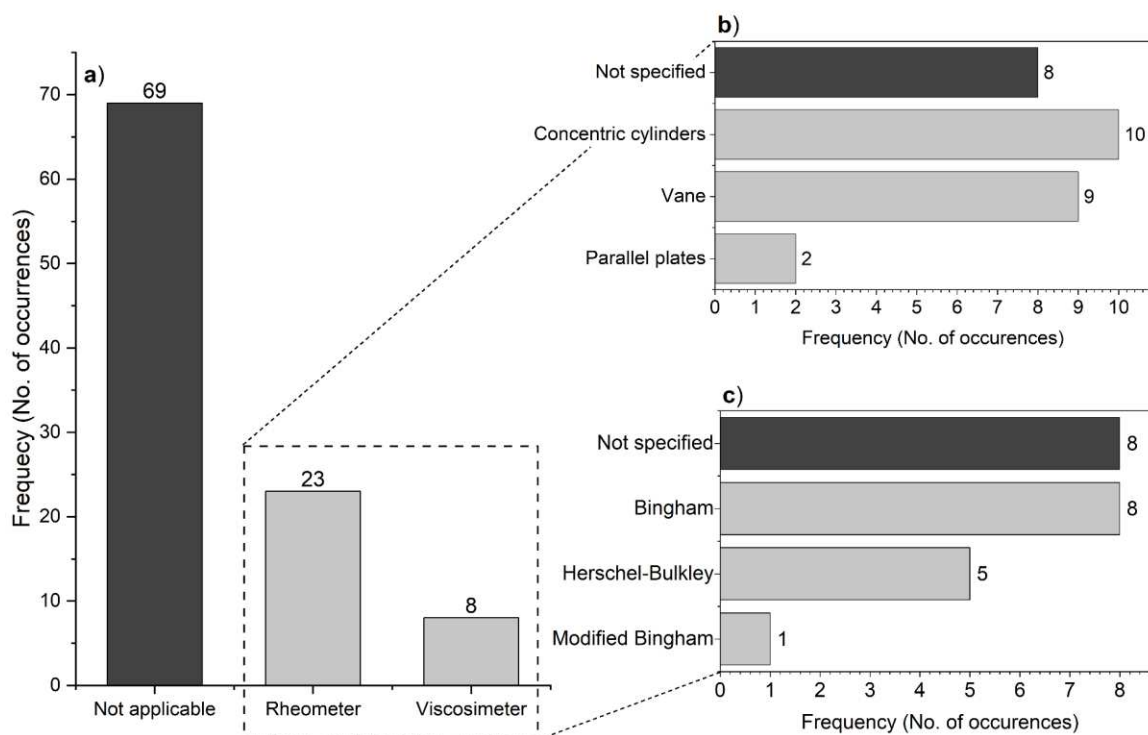


Fig. 11. Frequency of rheometry tests regarding (a) the equipment, (b) the rotor geometry, and (c) the rheological model used to obtain rheological parameters.

The analysis presented in Fig. 11c indicates that detailed rheological studies on AAMs, using pre-existing rheological models, are still in the early stages of development. The models employed are reported in only 14 studies from the systematic review. Specifically, 8 studies applied the Bingham model, 5 utilised the Herschel-Bulkley model, and 1 adopted the Modified Bingham model. The Bingham model, which assumes a linear relationship between shear stress and shear rate, is not the most appropriate for AAMs due to the changes in viscosity over time [48]. In contrast, both the Herschel-Bulkley and Modified Bingham models introduce parameters that account for the variation in viscosity with changes in shear rate, making them more suitable for assessing AAMs [49].

3. Advances in understanding the mechanisms of interaction between superplasticisers and particles in AAMs

Fig. 12 illustrates the main advances in understanding the interaction mechanisms between the superplasticisers and the precursor particles in AAMs. Discussions around this topic began around 2000 with Bakharev et al. [35], who investigated concrete with AAS, LS, and NP-based

450 superplasticisers. They proposed that chemical admixtures in the systems acted as nonpolar
451 molecules with attraction forces driven by Coulomb attraction between positively and
452 negatively charged particles. They suggested that this mechanism could explain LS's positive
453 effect on the workability of AAS systems. A few years later, some authors discussed some
454 evidence of the low efficiency of superplasticisers in AAMs when compared to Portland
455 cement systems.

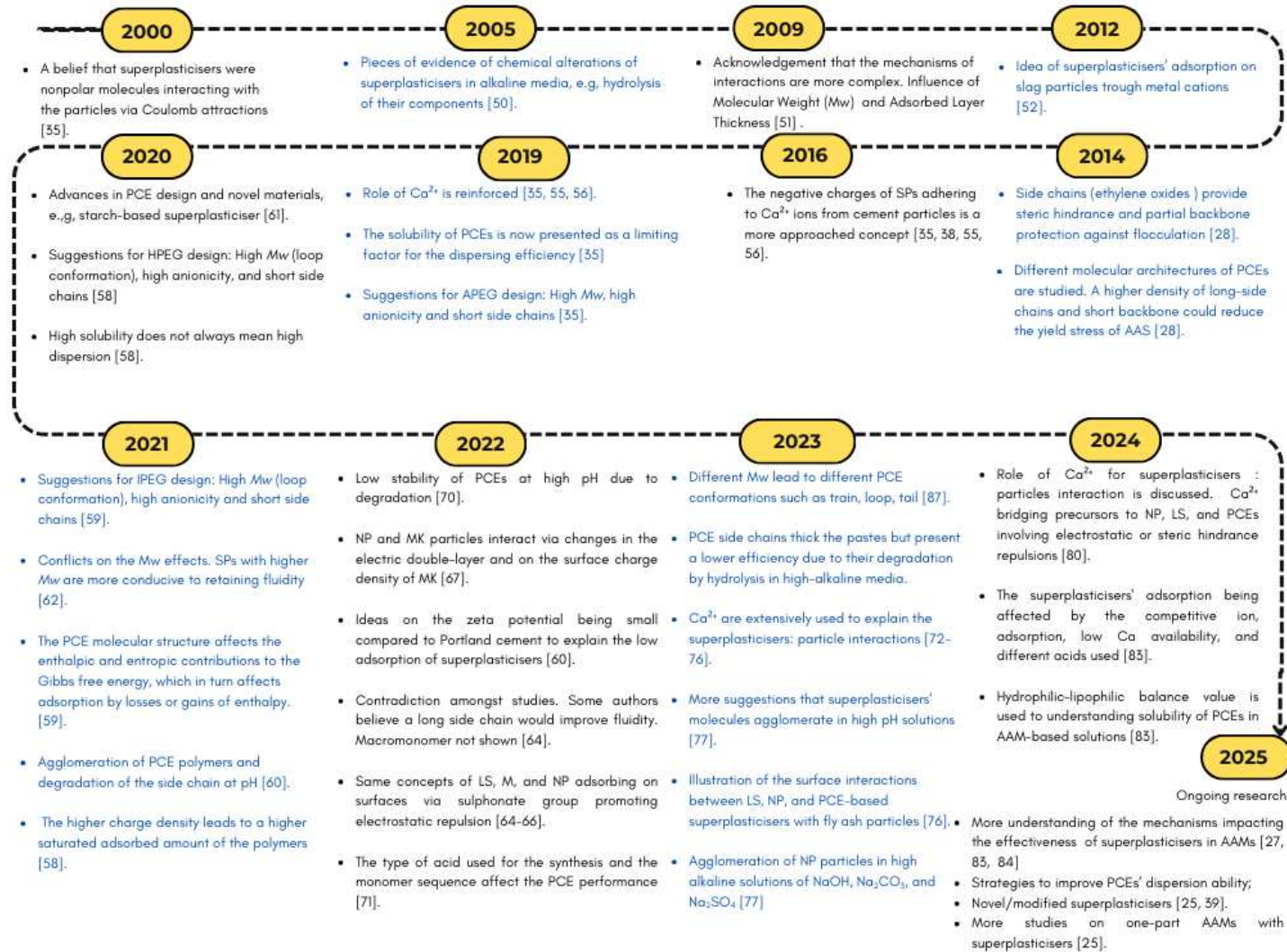


Fig. 12. Timeline of the advances in the interaction mechanisms between superplasticisers and AAM precursor particles.

In 2005, Palacios and Puertas [50] investigated the effects of five superplasticisers (PCEs, M, NP, and V-based) on the AAS pastes and mortars. Based on bands from Fourier-transform infrared (FTIR) spectroscopy, they concluded that all the superplasticisers underwent structural change in high pH solutions (13-13.6). For PCEs, the changes were observed due to the disappearance of the band corresponding to C=O in the ether groups (side chain) and the appearance of bands corresponding to COO of carboxylate groups (backbone). This evidence shows that after the carboxylate groups from the main chain are absorbed on the slag surface, the side chains break down due to hydrolysis, explaining the absence of steric hindrance in PCE. This mechanism promotes the dispersion of PCE in the PC system. According to the authors, the polymer structural change is also responsible for the loss of dispersion of vinyl copolymer-based SP, which is also observed in high alkaline media. This leads to the amide in part of the polymers undergoing hydrolysis to form amine observed in sulfonate groups and carboxylate salts. For M-based superplasticisers, slight alterations were observed, but they seemed more pronounced in the sodium silicate activator. The NP-based admixture was very stable in the NaOH solution, but when the alkaline solution contained sodium silicate, alterations in the SO₃ groups occurred.

Over the years, understanding the low efficiency of various superplasticisers in enhancing the workability of AAS has become more complex, with multiple factors influencing performance beyond solely the alkaline media. According to Palacios et al. [51], the type of superplasticisers and binder, dosage, and pH affect the rheological parameters. When using NP-, M-, or V-based superplasticisers in AAS, these admixtures impact the adsorption of slag particles by altering the zeta potential values and reducing the paste's yield stress to varying degrees. The study concluded that dispersion is linked to the M_w and layer thickness of the polymer on the slag particles, and more studies were needed. Yang et al. [52] also explored the adsorption of superplasticisers in AAS, contributing that metal cations mediate the superplasticiser adsorption on slag, i.e. Ca⁺², Na⁺, K⁺, and Mg⁺ cations could impact the adsorption and/or the electrostatic environment.

Due to the inherent complex chemistry of AAMs, the discussion was opened on investigating various molecular architectures of superplasticisers (mainly PCEs) and examining how their characteristics affect the rheological behaviour of AAMs. In 2014, according to Kashani et al. [28], a PCE polymer possessing a long backbone chain and a few short side chains caused an increased yield stress of AAS pastes up to 90% due to the more attractive interparticle forces and adsorption of multiple GGBFS particles. The opposite effect was observed for a short backbone polymer with a long side chain in which this strong attraction can be limited by the steric hindrance of the side chain, restricting each polymer adsorption to a few particles while protecting the backbone from flocculation. Other authors also agree that several side chains due to ethylene oxides ($-\text{CH}_2\text{CH}_2\text{O}-$) minimise flocculation in AAS mixes [53,54].

Since 2016, research has increasingly discussed the role of Ca^{2+} cations on the superplasticiser-particles interactions in AAMs. When anhydrous PC reacts with water, it releases Ca^{2+} into the pore solution. The negatively charged superplasticisers interact with positively charged ions, adhering their polymers to the particles' electrical double-layer (EDL), providing dispersion via electrostatic repulsion or steric hindrance. These interactions are known for promoting workability in PC systems. Nowadays, this concept is increasingly more consolidated to explain the interaction mechanism of LS-, NP-, and PCE-based in Ca-rich AAMs based on the reports of several authors [38,55,56]. In 2019, according to Conte and Plank [35], the high efficiency of APEG PCEs was due to their stronger interaction with calcium ions. The authors mentioned the role of dicarboxylate functionality of maleic anhydride, producing a high chelating effect on Ca^{2+} in systems with NaOH or Na_2CO_3 as activators. Contrary to the ideas of some authors [28,57], they also suggested that PCEs (e.g. APEG) with a long backbone chain and short side chain would achieve sufficient dispersion. Additionally, solubility was presented as the limiting factor for the dispersion efficiency of PCEs.

Since 2020, there have been advances in the design and synthesis of PCEs. Research is increasingly focused on deeper research on different macromonomers, such as MPEG, HPEG, and IPEG, exploring variations on M_w , side chain lengths, anionicity, and acid types. The findings indicated that high dispersion efficiency for certain macromonomers (e.g., IPGE, APEG, and HPEG) is linked to some specific molecular characteristics: high anionicity leading to stronger polymer adsorption, high M_w to improve the workability due to the PCEs adopting a loop conformation, and short side chains to reduce insolubility issues [37,58,59]. Lei and Chan [58] proved that high solubility does not always mean high dispersion, as the polymer needs, most importantly, to adsorb onto the particles. A year later, Lei and Zhang [59] discussed that these molecular characteristics significantly affect enthalpy and entropy contributions to the Gibbs free energy ΔG related to the PCE's adsorption, with anionicity being a crucial parameter. Discussions also suggested superplasticisers failing to EDL may undergo partial decomposition, insolubility, and agglomeration. Wetzel et al. [60] demonstrated the formation of PCE (APEG, MPEG) agglomerates in high-fluorescent spherical spots using concentrated water glass solutions. Additionally, novel superplasticisers such as starch- or methyl isobutyl carbinol-based superplasticisers has been studied to improve the workability of MK-based AAMs [61]. It is essential to note that the conclusions regarding the molecular architecture of superplasticisers are limited to the polymers, particles, and alkaline media tested. Ouyang et al. [62], for instance, defended that polymers with high M_w are more likely to reduce the fluidity of AAS due to the entanglements of main chains, which conflicts with ideas presented by other authors. More details on the effects of the PCE architecture on the dispersion of AAMs will be given in the following sections of this study.

In 2022, research intensified regarding the working mechanism between the particles and LS-, NP-, M-, and PCE-based superplasticisers and how the chemistry of the alkaline media strongly influences the adsorption and chemical stability of superplasticisers. In LS-based superplasticisers in AAS, Kalina et al. [63] described the interactions driven by electrostatic repulsion. The negative sulfonate groups in LS polymers adsorb on the positive surface of slag in the alkaline solution due to the deprotonation of silanol groups. The magnitude of the zeta potential depends on the slag's chemistry. The research findings are based on the efficiency of LS in different silicate modulus at 0-0.1 modulus. The LS is efficient in increasing workability, but as the silicate modulus increases to 0.25 and 0.50, there is a low efficiency, probably caused by the competitive adsorption of LS and silicate (from activators) onto slag surface.

Electrostatic repulsion is also the proposed working mechanism in NP- and MN-based systems [64–66]. However, some specific interactions, depending on the type of particles, can be described. For low-Ca (or free-Ca) systems such as FA or MK, the particles typically present a negative surface charge that becomes more negative as pH increases due to deprotonation of surface hydroxyl groups [60]. In the case of FA particles, some authors described the low adsorption of NP due to the low zeta potential compared to PC, and the smooth and negatively charged surface. In the MK particles, Derkani et al. [67] explained the fluidity of AAMs due to changes in the distribution and structure of the EDL, as well as structural forces, due to alteration in surface charge density and hydrated shell of MK, facilitating competitive adsorption of the polymer. The pH variations change the EDL as reported by Derkani et al [67]. The zeta potential values for MK particles in NaOH or KOH solutions shifted from -30.5 mV at pH 7 to -66.3 mV in NaOH at pH ~12. Beyond this point, dissolution of MK reduces the negativity of the zeta potential as Si and Al ions are released. The strong negative charges can reduce the adsorption of anionic functional groups in superplasticisers, unlike in PC or Ca-rich AAMs, where Ca^{2+} promotes positive surface charges and bridging. Also proven by the authors that Ca^{2+} ions increased NP-based superplasticisers more than Mg^{2+} .

In Ca-rich suspensions such as slags, zeta potential values vary widely with pH. At low pH (~2–3), slags are positively charged, but as pH increases, they become progressively negative until dissolution occurs at >12, releasing Ca^{2+} , K^+ , Na^+ , and OH^- ions, which shift the zeta potential to less negative or more positive values [68,69]. This dissolution increases ionic strength but also destabilises superplasticisers. Zhang et al. [70] showed that LS, NP, M-, and PCE-based admixtures lose stability at high pH, fragmenting into small molecules that reduce fluidity.

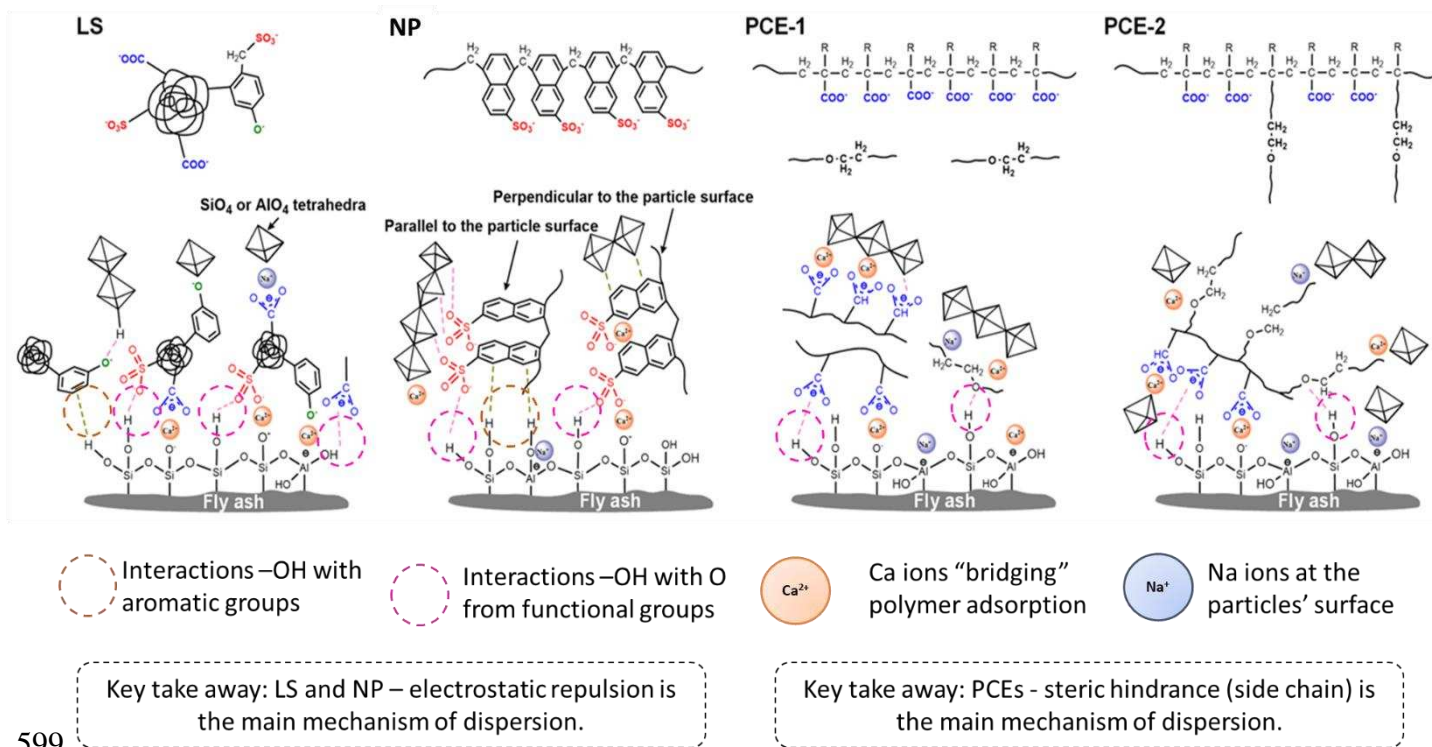
In the case of the PCE-based superplasticisers, steric hindrance caused by the side chain is agreed to be the main working mechanism for particle dispersion. The parameters influencing the adsorption of PCEs seem to be the focus of research in recent years. Studies on the acid type and monomer sequence also contributed to the progress in PCE studies. Li et al. [71] found that HPEG PCEs possessing AAA and AAE sequences (A=acid, E=ether) had superior dispersion than APEG PCEs. This strengthens the idea of macromonomers with various distributions such as random, block, gradient, etc, likely affecting the polymer conformation on the particles' surface. For those macromonomers, the presence of extra $-\text{CH}_3$ groups (from the methacrylate acid) is suggested as the methyl groups would enhance the stiffness of the polymers in alkaline media, mitigating particle agglomeration, and more anchor groups could be exposed to promote adsorption. Conversely to the previously observed about preferable short side chain length, Hita and Criado observed that one of the PCE had more effective fluidity due to the presence of very long chains [64]. The effects of the PCE molecular structure are discussed in the following sections.

In 2023, there were no changes in understanding the working mechanism between superplasticisers and particle AAM and polymer design. Vanitha et al. [72] studied FA/GGBFS systems with water glass, nano- SiO_2 , and modified carboxylate, agreeing with the role of Na and Ca ions, which charge the zeta potential charges to less negative values and help the adsorption of the superplasticisers. The plasticising effects of the modified polycarboxylate were also attributed to the long side chains. The role of Ca^{2+} in facilitating the binding of superplasticisers was cited by several authors in AAS studies with LS-, NP- and PCE-based superplasticisers [72–76]. On the other hand, there were advances in understanding the reduced dispersion ability of NP polymers in alkaline solutions. The formation of micelles is suggested by Tian et al. [77] as the mechanism explaining the agglomeration of NP polymers in solutions of NaOH, Na_2SO_4 , or Na_2CO_3 .

Wang et al. [76] illustrated the surface interactions between LS, NP, and PCE-based superplasticisers with FA particles (Fig. 13). Some of the interactions include weak hydrogen bonds between what they called pi-cloud in the aromatic group, silanol $-\text{OH}$ groups (brown dashed line), and other hydrogen bonds between the $-\text{OH}$ groups and oxygen in functional groups (e.g. sulfonate, carboxyl, phenolic, and polyethylene groups) (pink dashed lines). Ca^{2+} bridges the anionic functional groups of superplasticisers and oxygen. Some parts (monomers and oligomers) of superplasticisers find it hard to occupy all the reactive sites of the FA surface.

There is also a competition for reactive sites from superplasticisers and precipitate gels, which might delay reactions.

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Fig. 13. Interactions between superplasticisers and species in FA-based AAMs. Adapted from [76].

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Advances in imaging analysis, such as Transmission Electron Microscopy with Energy-dispersive X-ray (TEM/EDX), reported that agglomeration of NP particles in high alkaline solutions of NaOH, Na₂CO₃, and Na₂SO₄ [77]. The authors attributed NP's low efficiency in AAS to the formation of micelles, which is intensified by the reduced mobility of alkaline solutions with high ionic strength. This finding corroborates the understanding of the low efficiency of other superplasticisers, but further imaging analyses are needed to confirm the phenomenon in LS, M, and PCE-based superplasticisers.

Regarding PCE-focused studies, Partschfeld et al. [78] discuss the PCE side thickening of the mixtures of MMK-based AAM and the side chains of HPEG, IPEG, and MPEG in AAMs undergoing hydrolysis in systems activated by NaOH and KOH, potassium silicate, causing a jeopardised steric hindrance force. Su et al. [79] studied a recent type of copolymer, the TPEG PCE in slag NaOH-activated systems. The surface interactions revealed that high adsorption did not necessarily imply high dispersion. The finding agrees with the previously found for

NP-based studies, the TPEG PCE molecules were adsorbed on the particle surface as soluble aggregates and the side chain suffered hydrolysis in NaOH solution. Large amounts of Na^+ can shield the electrostatic interaction of the R-COO^- of the PCE molecule, resulting in more hydrophobic molecules in solution, their collapse and agglomeration. This conflicts with previous studies mentioning that Na^+ increased the superplasticisers' adsorption.

In 2024, Ca^{2+} ions are established as facilitators for superplasticiser adsorption. Recent findings reported by Zhang et al. [80] mention that the composition and concentration of Ca significantly affect the efficiency of various superplasticisers. The principal is believed to help the system with calcined clays such as AAMK or hybrid systems with Portland cement activated by NaOH [81,82]. However, the facility that Ca^{2+} ions interact with PCE depends on their chemical composition. Zhang et al. [83] observed that the MPEG synthesised with polyacrylate acid (PAA) demonstrated a higher Ca-binding capacity than those synthesised with methyl methacrylate acid (PMMA), due to the better coordination allowing the penetration of ion condensation. These authors also applied the calculation of the hydrophilic-lipophilic balance to measure the solubility of PCEs, corroborating the "cloud point" results.

The ongoing research in 2025 is increasingly focusing on understanding the mechanisms impacting the effectiveness of superplasticisers in AAMs (mainly PCEs in AAS), blending of PCEs with other superplasticisers to improve performance, one-part AAMs, and novel superplasticisers. Chen and Plank [27] proved by gel permeation chromatography that MPEG, HPEG, and EPEG-based PCE do not decompose under high alkaline conditions. In fact, the polymers go through agglomeration as suggested by the increasing size distribution as tested by dynamic light scattering analysis. As the alkaline concentration of NaOH and Na_2SiO_3 increased, the polymer size increased, leading to a "cloud" point where the solution becomes turbid, suggesting solubility issues reducing particle/polymer interactions. In some cases, the values at each of the PCEs reached the precipitation onset were around 3 M NaOH and 1M Na_2SiO_3 solutions. The mechanism used to explain this phenomenon is based on the *Hofmeister* series. NaOH creates a disordered (chaotropic) water environment that enhances polymer solubility as the polymer can freely dissolve, while Na_2SiO_3 forms an ordered (cosmotropic) 3D-like water structure that limits solubility. These challenges, when using Na_2SiO_3 , can be even more significant considering the use of liquid Na_2SiO_3 activators, as their high viscosity can thicken the pastes, decreasing the dispersibility of the superplasticisers. According to Kosenko, Wetzel, and Middendorf [84] the increasing alkaline concentration linearly decreases the polymer adsorption. At low activator concentration, the adsorption capacity of PCE on

FA/GGBFS surfaces can be improved if KOH activator is used due to K^+ anchoring PCE polymers onto the particle's surfaces.

Overall, current research indicates that the high ionic media of AAMs reduce the superplasticisers' efficiency due to the high pH, complex and high ion concentrations, ion competitions, and changes in the EDL. Specifically on this topic, Chen and Plank [27] recently investigated the influence of measured ionic strength and solution pH on the dispersion ability of PCE superplasticisers. They observed that increased ionic strength, directly related to alkali concentration, promotes the agglomeration of PCEs, described as a "coiling" process, which hinders both their solubility and performance. Although the authors did not analyse the coiling mechanism in detail, they highlighted it as a key area for future research. This proposed behaviour aligns with findings reported in other recent studies [25,85]. However, the detailed impact of such micromechanical calculations on the rheology of AAMs has not yet been investigated.

Once the low dispersion capacity of PCE in AAMs has been stated, strategies have been proposed to improve their performance. Su et al. [39] showed positive compatibility of PCE-based superplasticiser with sodium gluconate retarder in AAS system as a strategy to improve retention of AAS, which is rapidly lost. Sha, Wang, and Ye [25] opted to use phosphate-based superplasticisers in AAS. According to this review, the study focuses on a poorly explored area of AAMs: the one-part AAMs, which consist of mixes where only water needs to be added to the blended mix of dry activators. Using K_2CO_3 or K_2CO_3+CaO as an activator, the author suggested that the loss of effectiveness of phosphate-based superplasticiser is due to limited solubility in alkaline media or competition with carbonate ions for adsorption sites on slag surfaces, which supports the hypothesis of changes in the polymer conformation. The overall summary of the recent knowledge advances considering the interaction mechanisms between superplasticiser admixtures and precursor particles is presented in Table 1.

Table 1. Summary of the advances in the interaction mechanisms between superplasticisers and AAM precursor particles.

Topic	Superplasticiser			Status
	LS-based	NP-based	PCE-based	

Mechanism/ interaction	Electrostatic repulsion (hydrogen bonds between the –OH groups of the particles' surface and oxygen in functional groups (e.g. sulfonate, carboxyl, phenolic, and polyoxyethylene groups) or –OH groups with aromatic groups. [76]	Steric hindrance (Carboxyl groups adsorb onto the particle surface while side chain (polyoxyethylene groups) promote dispersion by steric hindrance. [76]	Well-known	
Role of Ca (adsorption) in high-Ca systems (e.g. GGBFS)	Adsorption facilitated by Ca ²⁺ ions bridging [63].	Adsorption facilitated by Ca ²⁺ ions bridging. [73]	Adsorption facilitated by Ca ²⁺ ions bridging [37]	Well-known.
Role of Ca (adsorption) in low-Ca (or free-Ca) systems (e.g. MK and FA)	Studies were not found or did not explicitly state the role of Ca ²⁺ facilitating adsorption.	Adsorption due to changes in the EDL of the MK surface. Adsorption facilitated by Ca ²⁺ ions bridging, if Ca is present [67]. In FA particles, adsorption is facilitated by Ca ²⁺ ions bridging, if Ca is present [63].	Adsorption facilitated by Ca ²⁺ ions bridging, if Ca is present [63].	Needs further investigation
Surface charge and pH	At high pH solutions, GGBFS and MK surfaces become more negative, which can reduce the adsorption of anionic groups/ superplasticisers [67–69]. Dissolution releases ions that modify the zeta potential. However, the effects of different superplasticisers altering the zeta potential charges of different particles are unexplored.			Needs further investigation.
Effects of molecular architecture	Not found		Backbone, Acid (type, motif), macromonomers, <i>M_w</i> , Charge density, side chain, etc.	Needs further investigation.
Key limitations	Often exhibits lower dispersion compared to other superplasticisers. efficiency drops as Na ₂ SiO ₃	Micelle-like formation (agglomeration) and poor chemical stability in Na ₂ SiO ₃ ,	Micelle-like formation (agglomeration), poor chemical stability in high-alkaline solutions, solubility issues (cloud point), and lower	Needs further investigation.

concentration increases due to polymer competition for adsorption [63].	NaOH, Na ₂ CO ₃ solutions [76,77].	efficiency compared to PC systems. Uncertainties remain on the effect of varied molecular structures [27,58,60].
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676 4. Influence of the chemical structure of PCEs and their interrelationships in AAMs

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678 4.1. Influence of the macromonomers

679 A macromonomer refers to a macromolecule containing oligomeric or polymeric chains,
680 characterised by a polymerisable end-group [86]. Over the last decades, several types of PCE
681 macromonomers have been developed, including MPEG, APEG, VPEG, HPEG, IPEG, etc.
682 [35]. Fig. 14 shows an example of different chemical structures of PCE such as APEG, HPEG,
683 IPEG, VPEG (VMA = viscosity-modifying admixture), EPEG, GPEG, according to Lei Lei,
684 Hirata and Plank [21]. The differences amongst them refer to the type macromonomers used in
685 the PCE synthesis. The subscript letters “a”, “b”, and “n” refer to the numbers of carboxylate
686 groups in the backbone, neutral backbone units, and the numbers of repeating PEG units in the
687 side chain, respectively. The part “c” in the VPEG admixtures correspond to a number of vinyl
688 ether units.

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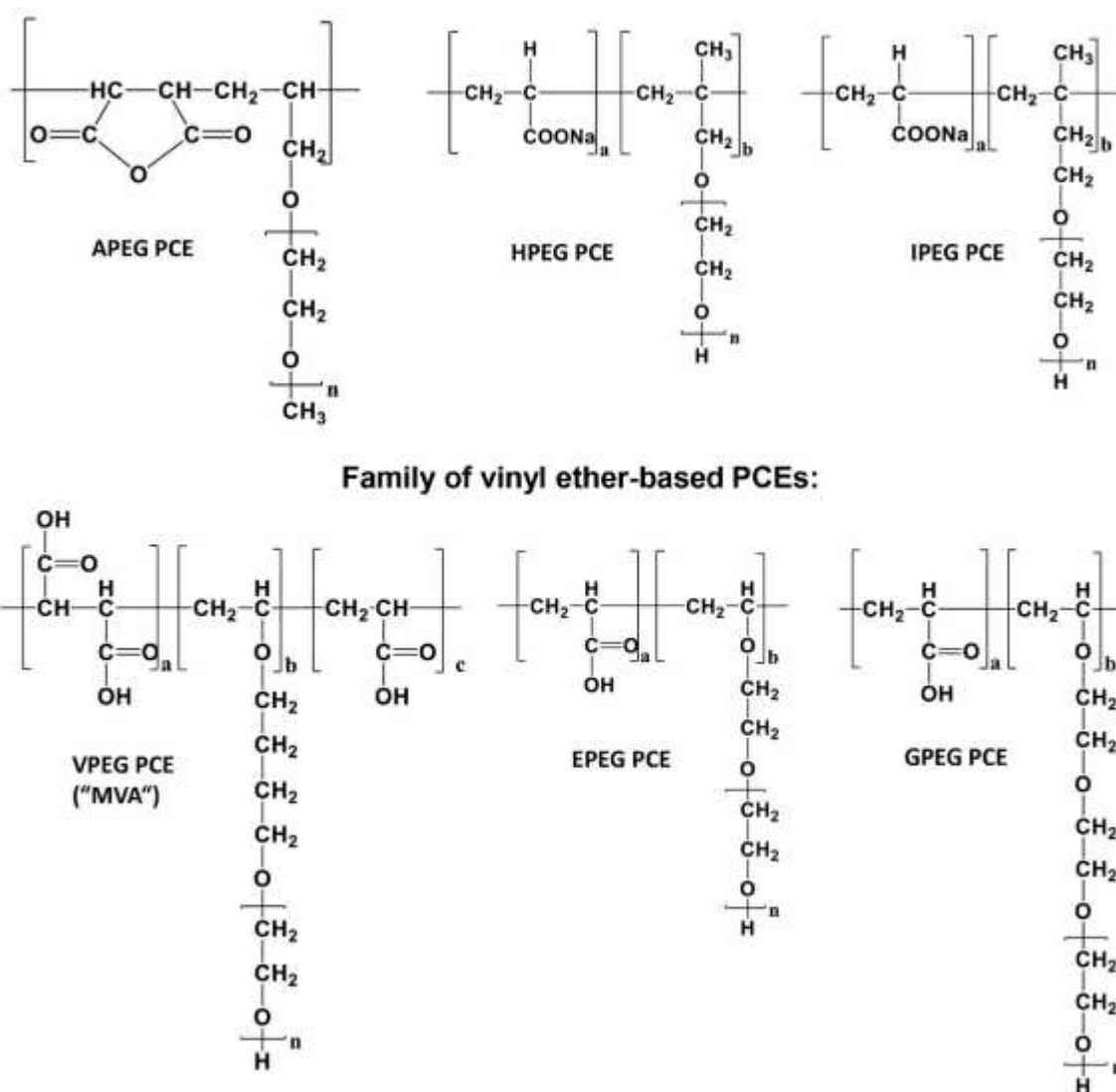


Fig. 14 Chemical structures of PCE polymers. APEG, HPEG, IPEG, VPEG, EPEG, GPEG PCEs from [21]

Research has shown that dispersion effectiveness depends not only on the chemistry of the macromonomer (which represents the side chain precursor, used to graft polyethene glycol (PEG) chains onto the backbone of PCEs) but also significantly on other factors such as the type of precursors in AAMs, characteristics of the chains (M_w or side chain length), etc. For high-calcium systems (such as AAS), Conte and Plank [37] studied the dispersion efficiency of MPEG, APEG, IPEG and phosphate polymers with different molecular structures. They observed that APEG-PCE with a shorter side chain ($n_{EO}=7$) and high anionicity and molecular weight ($>30,000$ g/mol, M_w) produced a superior dispersion in NaOH-slag systems. Additionally, these polymers had no efficiency for Na_2CO_3 -slag systems. Although the positive performance of APEG, Lei and Chan [58] relate that these polymers are rarely produced by the industry, especially under such a low side chain, which impairs their wide use.

MPEG and phosphate polymers seem less efficient than APEG, and there are only a few studies on IPEG for AAMs. Lei and Zhang [59], synthesising different IPEG PCE characteristics, demonstrated that the dispersion ability also increases with anionicity for the same side chain length and a short chain ($n_{EO}=7$). However, the production of IPEG relies on the availability of high-quality isoprenol, which limits its increasing manufacture [59]. These reasons have encouraged more investigation towards the use of HPEG polymers.

With more HPEG-oriented studies, Lei and Chan [58] synthesised a series of HPEG PCE polymers with different anionicity and side chains to gain more insights into this type of PCE. As well as observed for APEG, it was possible to establish a connection between a higher dispersion ability with the high M_w , high anionicity and short side chains of the PCEs in NaOH-activated slag binders. When HPEG- and APEG-PCEs were compared in a study by Li et al. [71], HPEG PCEs exhibited superior dispersion over APEG, especially at high anionicity due to its stronger adsorption of these polymers on slag's surface. No research was observed on the effects of different macromonomers on the performances of PCE-based superplasticisers for Ca-free AAMs (such as MK-based geopolymers), nor testing other macromonomers such as VPEG (EPEG or GPEG), which highlights that more research is needed in this area.

4.2. Influence of different acids

Acids are often used as catalysts in polymerisation reactions during PCE production. They alter the reactivity of PCE by including carboxylate groups, extra functional groups, and they influence the polymer interactions with the ions in the pore solution. The type and motif (pattern) in which the acids are arranged in the backbone result in different behaviours depending on the macromonomers. MPEG-PCE polymers synthesised with acrylic acid (AA) and methacrylic acid (MAA) were investigated in AAS systems by Zhang et al. [80]. The authors observed that AA polymers provided greater Ca^{2+} binding than MAA polymers due to the coordination numbers provided by the AA polymer chain, resulting in a high fluidity of AAS samples. In the MAA, the methyl group of MAA polymers could prevent the penetration of divalent cations and ion condensation, explaining the reduced binding capacity. Contradictory, a positive effect of the methyl group was observed in more recent polymers such as HPEG in a study by Li et al. [71]. According to the authors, introducing a methyl group increases the backbone stiffness, resulting in less shrinkage, i.e. less agglomeration, and a more linear stable structure with more available anchor groups, so AA would be preferable. For APEG PCE polymers, Zhang et al. [74] observed that maleic anhydride acid (MA) provides a stronger Ca^{2+} binding than acrylic acid (AA) under similar anionicity and M_w of APEG-PCE

in AAS systems. However, it is important to note that this performance is associated with the amount of Ca^{2+} and $-\text{COOH}$ in the system and these studies were all conducted in AAS.

Another factor regarding the acids is their arrangement with the ether segments in the backbone molecule. Li et al. [71] observed that HPEG PCEs possessing AAA and AAE (A: acid and E: ethers) monomer sequences presented enhanced dispersion capacity than APEG PCEs with EAE sequence. The possibility of working on tailoring PCEs under different motifs opens more chances to increase the PCEs' performance. Random, alternating, block, and graft sequences are examples of settings and may impact different polymer conformations on the particles' surfaces.

4.3. Influence of the Molecular Weight (M_w)

Another key parameter to be considered in PCE polymers is the M_w . One of the first mentions of M_w affecting the dispersion capacity of AAM samples was given by Palacios et al. [51]. They suggested that the high dispersion capacity of vinyl copolymers in AAS was due to the steric contribution from the adsorbed layer thickness linked to a high M_w (>28,000 Da). However, no solid evidence of this phenomenon was presented at that point. Studies varying PCE polymers such as HPEG, APEG and IPEG for AAS-based systems also observed the positive effects of high M_w . Lei and Chan [58] synthesised HPEG PCE with different M_w for AAS systems. They concluded that the higher the M_w , the better the dispersion of HPEG-based PCE. Studies on PEG polymers have shown similar performance. Conte and Plank [37] studied APEG-based PCEs, which presented the highest spread flow among IPEG, MPEG, and phosphate superplasticisers. They found that APEG-based PCEs possessing what they considered a high M_w (>30,000 Da) and comparable side chain length had the highest dispersion capacity.

In the same year, Li et al. [87] produced polymers possessing the same anionicity and side chain but varied M_w (13,000-400,000 Da) in AAS. Results from dynamic light scattering and TEM images proved the higher the M_w the thicker the adsorbed layer of the polymers on the GGBFS surface. This study introduced an interesting concept of polymer conformation. According to the authors, a high M_w would favour a tail-like conformation of the polymers on the particles, increasing the distance (dispersion) between the particles, as illustrated in Fig. 15. This would explain the high dispersion of cement particles when PCE-based superplasticisers of high M_w are used. However, the interactions of multiple molecules and a more realistic polymer size should be considered, as they might influence the dispersion performance, which

is commonly one of the limitations of simplified systems of a single molecule presented in computational simulations.

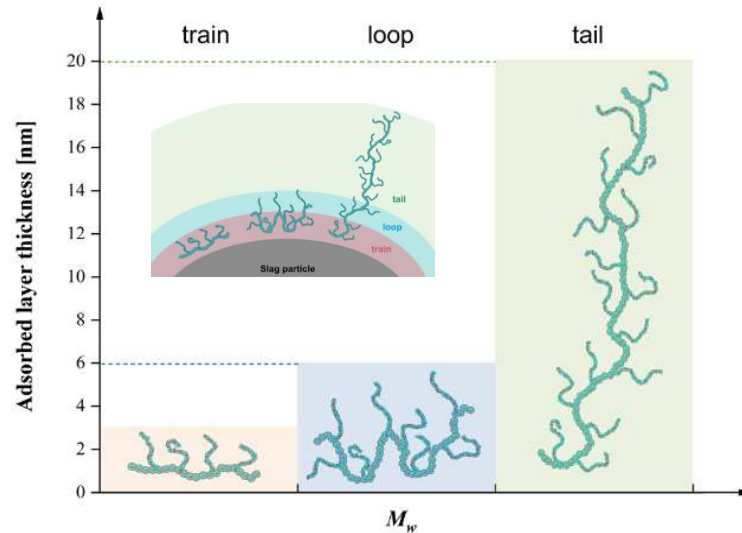


Fig. 15. Schematic representation of different conformations of PCE polymers onto the slag surface based on the increasing M_w . Adapted from [87].

The uncertainties regarding the role of M_w remain not fully understood. While a high M_w can contribute to creating a dense and more resistant polymer, increasing the adsorbed layer thickness, and influencing the conformation of polymers on the surface of particles, further research is needed. The effects of M_w in different superplasticisers, such as LS- or NP-based ones, have not been reported, nor has the conformation of polymers under different alkaline solutions.

4.4. Influence of the side chain and charge density

There is debate on the effects of charge density of the backbone and PCE side chain length on the dispersion of AAMs. The charge density of the PCE backbone, related to the acid-to-ether ratio, influences their adsorption on the binder surfaces as well as the side chain length as illustrated in Fig. 16. According to Plank, Sachsenhauer and de Reese [88], the thermodynamic parameters involved in the polymer adsorption occur due to two main energy effects that determine the Gibbs-free energy change (ΔG): the enthalpy (ΔH) or the entropy of adsorption (ΔS). The enthalpy of adsorption involves attraction between particles (PCE: surfaces) (positive and negative charges), which releases energy ($\Delta H < 0$); when the PCE attaches to the surface, there is an increase in entropy as counter-ions and water molecules are released in the pore solution upon adsorption ($\Delta S > 0$). Thus, both parameters contribute to absorption and the

balance between them is influenced by the PCE molecular structure (e.g., charge density, side chain length, etc.). Increasing the charge density (enthalpy contribution) can increase the polymer adsorption. According to Lei and Zhang [59], a high charge density always leads to a highly saturated adsorbed amount of polymers on the particles' surface. The authors found that IPEG PCE polymers of high charge density for polymers of the same side chain length had higher saturated adsorbed polymer on the particles' surface.

The effects on the side chain length seem to vary according to the type of macromonomers. Lei and Zhang [59] observed that IPEG PCE possessing longer side chains had better dispersion ability than the ones with shorter side chains, even though the longer side chain polymer had a higher absorbed amount of PCEs. The authors attributed the phenomenon to the low solubility of the polymer with a higher number of ethylene oxide units, which determines the side chain length, which also agrees with Conte and Plank in another study [37] that found a positive effect of side-chain length on the dispersion ability of alkali-activated materials with GGBFS when using APEG PCEs. A similar behaviour was also recently identified for HPEG [58] PCEs.

On the other hand, the beneficial effect of the long side chain was observed by Su et al. [79] studying TPEG PCE. The polymers possessing long side chains ($N_{EO}=53$) had better dispersion ability than the samples possessing short side chains ($N_{EO}=10$) for different charge densities (15, 30, 60) in NaOH solution (2 M). The authors attributed this behaviour to the steric hindrance effect from the PCE side chain, promoting the dispersion between the particles even for polymers with long side chains but low side-chain density. For the same side chain length, the higher the charge density (acid-to-ether ratios), the better the samples' dispersion ability; e.g. P53-60 > PC53-30 > P53-15, where P is a PCE polymer, 53 is the side chain length ($N_{EO}=53$), and 15,30,60 are the acid-to-ether ratios. A recent paper [64] also observed an increased dispersion ability when a PCE-based superplasticiser with long side chain length was used, but no information was given regarding the macromonomers. To summarise, both entropy and enthalpy contribute to the adsorption. High polymer adsorption does not always mean high dispersion ability, showing the importance of complementary tests. The effect of side chain length can vary significantly depending on the PCE polymers.

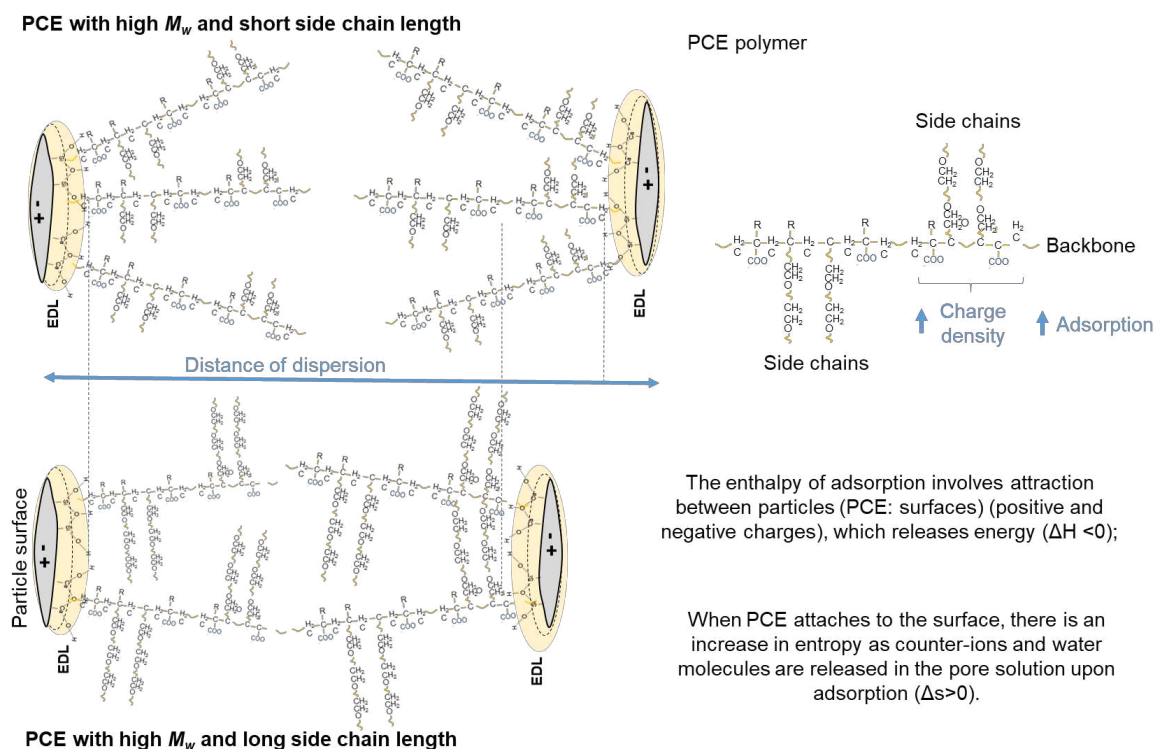


Fig. 16. Schematic representation of the effects of the side chain length and Gibbs energy involved.

4.5. Interrelationships amongst the molecular characteristics of PCE

The parameters defining the molecular structure of PCEs, such as M_w , macromonomer, side chain length, charge density, and type of acid and its sequence along the backbone, are interrelated and collectively determine the dispersion ability and chemical stability of PCEs in alkaline media. Increasing the M_w typically results in a longer main chain and often a greater number of side chains, which can influence charge density and steric hindrance. The longer the side chains, the higher the M_w . The length of the side chain can alter adsorption, steric hindrance, and conformation, as previously discussed. The side chain also controls the solubility as the presence and length of hydrophilic groups (such as polyethene glycol, PEG) determined by hydrophilic-lipophilic balance [80]. The charge density is linked to the number of carboxyl groups per unit of polymer chain; thus, this parameter correlates to the macromonomer and acid used for polymer synthesis. High charge density (high acid-to-ratio) means more carboxyl groups per chain length, which may reduce side chain spacing and steric hindrance. Conversely, low charge density means fewer carboxyl groups and more side chains, which might result in lower adsorption and increased steric hindrance. The macromonomer type is directly related to the side chain, as different macromonomers can be used to graft the

side chain to the polymer backbone. The acids are used for PCE synthesis with different macromonomers, affecting adsorption and backbone stiffness of PCEs, as previously discussed. The structural motif (acid sequence) determines the monomer sequence and position of side chains. This can affect how the backbone can adsorb on the particles' surfaces. According to Li et al. [71], HPEG PCEs with AAA*/AAE** dominant monomer sequences are preferable compared to APEG holding EAE main monomer sequence (*A=acid monomer; *E=ether). The effects of the different parameters of the molecular structure of PCEs and their interrelationships are presented in Table 2.

Table 2. Functions of different parameters of the PCE molecular structure and their interrelationships

Parameter	Effect	Interrelationship with other parameters
M_w	Defines polymer size chain, adsorbed thickness layer and conformation on the particles' surface	More side chains grafted, changes the distribution of charged density along the backbone
Side chain length	Controls steric hindrance and solubility	Longer side chains increase M_w ; overall, it is related to the structural motif
Anionicity/ charge density	Governs adsorption ability and electrostatic repulsion	Interrelated to acid and ether, and macromonomer choice
Macromonomer	Determines graft sites, backbone flexibility	Sets a range of M_w and side chain grafting patterns
Acid (synthesis of backbone)	Used for PCE synthesis with different macromonomers, affects adsorption, and backbone stiffness	Together with the macromonomer type, it affects side chain grafting sites, charge density and backbone stiffness
Structural motif (sequence of monomers)	Controls the distribution of charged groups along the backbone, and how it adsorbs onto the particle surface	It is linked to macromonomer design, alters charge density

4.6. Recommendations for the molecular structure of PCE polymers

An alternative to tackling the lower effectiveness of chemical admixtures in AAMs is the design and synthesis of novel chemical admixtures with structural modifications. PCEs can be tailored with different molecular characteristics/architectures (anionicity, main chain length, side chain length, M_w , etc.), and the investigation of which effects different parameters have on the performance of AAS systems has been a focus of many studies [37,58,59,71,87,89]. Table 3 presents the main findings on tailored PCEs to AAS, which can serve as a guide for PCE design. It is important to note that these results are based on specific formulations; consequently, the behaviour of PCE is likely to change depending on the mix proportions and type of precursors. Additionally, the effects of these parts of the PCE molecular structure are interrelated and together determine the performance of a superplasticiser. Therefore, additional research is needed to evaluate diverse activators and precursors across a range of PCE molecular structures.

Table 3. Recommendations for PCE tailored for AAS.

Details	Recommendations for polymer design	Refs.
Acid (synthesis of backbone)	Methacrylic acid (MAA) is recommended for MPEG	[80]
	Acrylic Acid (AA) is recommended for HPEG	[71]
	Maleic Anhydride Acid (MA) is recommended for APEG	[74]
High M_w,		
M_w	~400,000 Da M_w for HPEG	[87]
	>30,000 Da M_w for APEG	[37]
	>90,000 Da for IPEG	[59]
Anionicity	High Anionicity (~7) for HPEG	[58]
	High Anionicity (~7) for APEG	[71]
	High Anionicity (~15) for IPEG	[59]
Short side chains		
Side chain	$n_{EO} = 7, 10$ is recommended for HPEG	[58]
	$n_{EO} = 7$ is recommended for IPEG	[59]
	$n_{EO} = 7$ is recommended for APEG	[37]

Long side chain

$n_{EO} = 53$ is recommended for TPEG

[79]

Structural motif (sequence of monomers)	HPEGs with AAA*/AAE** dominant monomer sequences are preferable compared to APEG holding EAE main monomer sequence. (*A=acid monomer; *E=ether)	[71]
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865 **5. Performance of superplasticisers on the fresh state of AAMs**

866

867 **5.1. Ground-granulated blast furnace slag-based systems**

868 Over the last decades, numerous studies have been conducted to understand the effects of
 869 superplasticisers on the flow characteristics of PC systems. The ongoing research on the
 870 performance of different superplasticisers in AAMs demonstrates the challenges associated
 871 with examining this topic. An almost non-systematic behaviour of superplasticisers in AAMs
 872 is observed when analysing samples' flow characteristics, since the effect of superplasticiser
 873 varies greatly.

874 Such variation might be caused by variations in the type and composition of raw materials
 875 (precursors and activators), synthesis parameters (e.g., type of activator, concentration of
 876 materials, and water-to-binder ratio), and pH, among other factors. An additional factor that
 877 may significantly influence the performance of superplasticisers in AAMs is the distinction
 878 between two-part and one-part systems. The stability and efficacy of superplasticisers in these
 879 differing activation environments are not yet fully understood and remain underexplored in the
 880 current literature, highlighting a critical research gap that warrants further investigation. This
 881 is highly relevant due to a few articles that were found using one-part AAMs.

882 There are some uncertainties about which superplasticisers have the highest performance for
 883 AAS systems. According to the literature review, the superplasticisers improve to some extent
 884 the dispersion of AAS but not as much as in PC mixes [90]. For NaOH-AAS, NP-based
 885 superplasticiser has presented a good option as a dispersant polymer. Palacios and Puertas [50]
 886 studied the performance of five different superplasticisers (PC, M, vinyl copolymers and NP)
 887 in NaOH and Na₂SiO₃ solutions. Compared to the reference sample (no superplasticiser), NP
 888 showed enhanced workability, increased compressive strength and delay in the initial/final

setting times. Based on FTIR analysis, the authors attributed these results to the higher stability of these NP-superplasticisers in a high alkalinity environment, which breaks down other structures of superplasticisers, e.g., PCE-based. The effectiveness of NP in AAS was also recently reported by Tian et al. [77] for various activators. In this study, the NP-based superplasticiser had the worst performance in systems activated by NaOH.

In an additional evaluation on the use of NP-based superplasticiser in AAS, Palacios et al. [51] observed that the incorporation in two different contents (0.42 mg/g and 1.26 mg/g) resulted in the lower plastic viscosity and yield stress of pastes within a 13.6-pH NaOH-activated system when compared to reference (no superplasticiser), ML and vinyl copolymer superplasticisers samples. In turn, when analysing low-pH systems, all three superplasticisers investigated resulted in very similar results, reducing the yield stress when compared with the reference sample but on a similar scale. The effect of NP-based superplasticisers on the yield stress of AAS, as discussed by Palacios et al. [51], is summarised in Fig. 17.

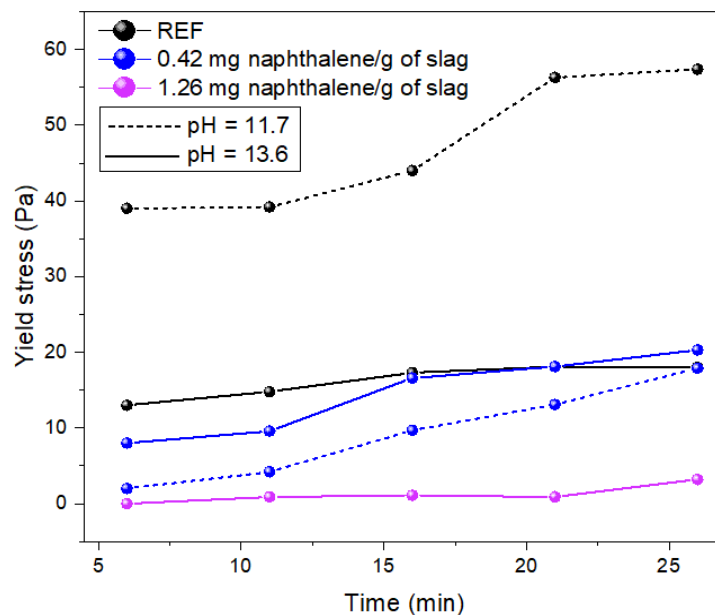


Fig. 17. Effect of NP superplasticiser on the yield stress of AAS. Adapted from [51].

However, sometimes NP is not the best option between the superplasticisers in NaOH-AAS. Although Luukkonen et al. [55] had observed that LS, ML and NP could improve the workability of the mixes when compared to PCEs in one-part AAS, LS had the best performance. The used LS significantly improved the workability (+41% spread, -51% yield stress, -27% viscosity), increased setting time (+70%), and enhanced compressive strength (+19%) results at a 0.5 wt% content. This behaviour may be associated with LS stability in the

alkaline environment, which allows the function of LS to provide repulsion between the particles, delay setting, and increase mechanical strength.

Considering the adoption of PCE-based superplasticisers, Paillard et al. [85] evaluated the impact of these admixtures on the rheology of AAS pastes. Their study focused on slags activated by Na_2CO_3 and NaOH , and the produced pastes were well-described by the Herschel-Bulkley model. Also, the paper revealed that the superplasticiser enhanced its efficiency (i.e., reduced yield stress) as the alkali dosage decreased. This finding suggests that the interaction between sodium ions and the superplasticiser's structure negatively affects its dispersion capability. However, these negative effects of sodium presence on superplasticisers' performance need further investigation.

Similarly, Tian et al. [77] investigated NP-based superplasticisers. The authors noted that NP-based superplasticisers showed increased efficiency at lower alkali dosages ($< 1\% \text{ Na}_2\text{O}$), aligning with [85]. Nonetheless, in practical applications, this lower alkali content is typically insufficient to fully engage the activation reactions. Therefore, under common alkali contents used in AAS systems, the observed efficiency of NP-based superplasticisers is not adversely affected by the alkali content. Another study [85] compared the performance of the superplasticiser in AAS systems with that in systems containing only slag and water, with no alkaline solution involved, to isolate the effect of the activator solution. The results indicated a significant loss of efficiency in the AAMs, particularly in the Na_2CO_3 -activated slag, where the effectiveness of the superplasticiser was nearly completely diminished and the yield stress measurements significantly increased. In turn, the yield stress of water-slag systems resulted in values near zero. The authors concluded that optimising the efficiency of superplasticisers is primarily dependent on the nature of the activator solution.

The performance of PCE in AAS remains uncertain, and a recent study conducted by Liberto et al. [91] provided valuable insights into the influence of ion presence on the superplasticiser's effectiveness. The authors conducted small oscillatory rheological tests to observe the impact of PCE addition (at a fixed content of 0.25 wt.%) in both PC and AAS. The results indicated that PCE performed poorly in AAS, with no significant effect on the cohesion parameter (i.e., linear elastic modulus). However, the study explored the effect of additional calcium on the rheology of AAS, provided by CaCl_2 . The incorporation of calcium in the range of 0 to 20 wt.% significantly enhanced the performance and dispersion ability of the PCE superplasticiser in AAS systems. According to the authors, the observed behaviour is attributed to surface

modification of slag particles, which causes variations in charge, density and potential, further modifying the particles' interactions.

Given the absence of a consensus on the best superplasticiser option for AAS, some researchers have recently investigated the use of PCE in AAS systems. Although apparently, these admixtures may not be as efficient as the previously mentioned ones and they can be designed with different chemical characteristics (anionicity, main or side chain length, chemical structure, etc.). Such variations in the chemical characteristics are critical to the performance of PCE-based superplasticisers and may enhance their dispersion ability.

Kashani et al. [28] investigated the impact of the molecular architecture and content of PCE superplasticisers on the rheological properties of AAS. The authors found that AAS pastes with PCE incorporation were well-described by the Herschel-Bulkley rheological model. They observed a reduction in the power index (n) with increasing PCE content, which indicated a transition towards more shear-thinning behaviour. According to the study, the length of the side chains of the PCEs plays a crucial role in the rheology of AAS pastes. Specifically, an increase in side chain length led to lower yield stress values at a 1:5 ratio of backbone charges to side chains, enhancing particle dispersion. This behaviour, as previously discussed, is associated with the steric forces caused by PCE molecules/chains. Both anionic and cationic PCEs exhibited similar trends concerning the effect of side chain length.

The study [28] also examined the effect of polymer molecular weight on the rheology of AAS. Higher molecular weights resulted in increased yield stress for both anionic and cationic backbones, particularly with a moderate side chain length ($N_{EO} = 22$), which adversely affected the particle dispersion mechanism. The effects of backbone charge were similar for both cationic and anionic PCEs, indicating that molecule charges are not significant, considering the effect of slag particles in an alkaline environment.

From the same point of view, the molecular architecture of PCE polymers was recently investigated by Zhang et al. [80]. The research involved synthesising admixtures using two different acid monomers: MAA and AA. The study revealed significant differences in performance between the two types of superplasticisers, indicating that the content and general type of superplasticiser (e.g., PCE, NP, LS, and M) alone are insufficient to fully understand their efficiency. Results showed that MAA-based superplasticisers performed markedly worse than AA-based ones, as evidenced by mini-slump and rotational rheometry tests. MAA-based systems increased the plastic viscosity of the pastes compared to the reference sample, thereby

reducing the flowability of the mixture. In contrast, AA-based systems demonstrated favourable rheological properties, significantly lowering both yield stress and viscosity relative to the reference (without superplasticiser) mixture.

From an overall perspective, the effect of superplasticisers in AAS systems has been extensively studied, as discussed in this section. Based on the reported findings, Table 4 summarises the mix designs, results, and key conclusions from the studies, aiming to provide the most important information and guide future research. Furthermore, the differing behaviours and insights presented in the literature underscore the need for additional studies to enhance understanding and progress in the use of superplasticisers in AAS. This table highlights different types of variables, underscoring the variety of parameters that could affect the efficiency of superplasticisers in AAS, such as activator type, solution pH, superplasticiser type and dosage, superplasticiser molecular architecture, among others. Also, the Herschel-Bulkley model was reported to well-describe the AAS samples independent of the superplasticiser type adopted, as previously discussed.

988

989 **Table 4.** Reported effects of superplasticiser in AAS rheology and workability.

Ref.	Activators	Superplasticiser type	Type of analysis	Rheological model	Main conclusions
[50]	NaOH, Na ₂ SiO ₃	PCE, NP, MN, V**	Mini-slump	-	Enhanced efficiency for NP-based SP. The remaining superplasticisers exhibited poor performances
[51]	NaOH	NP, MN, V*	Rotational rheometry	Not reported	- System's pH significantly alters the superplasticisers efficiency - In higher pH (13.6), NP exhibited the best results, reducing both yield stress and plastic viscosity measurements
[77]	NaOH, Na ₂ SO ₄ , Na ₂ CO ₃ , Na ₂ SiO ₃	NP	Mini-slump	-	- Viscosity of sodium silicate activator reduces the efficiency of NP due to the reduced diffusion and adsorption. - NP-based superplasticiser is more stable in Na₂SO₄ and Na₂CO₃ systems, being less stable (i.e., lower solubility) in the NaOH and Na₂SiO₃ solutions
[55]	NaOH	PCE, LS, MN, NP	Mini-slump and rotational rheometry	H-B*	LS exhibited the better performance, reducing the yield stress, viscosity and setting time of the AAS pastes

					- Optimised dosage of LS at about 1 wt.% - Reduced performance of PCE are attributed to the instability in high-pH systems
[85]	NaOH, Na ₂ CO ₃	MPEG PCE	Rotational rheometry	H-B*	- Activators anions plays a crucial role altering both dispersion, adsorption and conformation of the molecules - Low-sodium activation led to enhanced efficiency of the superplasticisers, increasing the reduction of yield stress and benefiting the workability
[91]	Na ₂ CO ₃	PCE	Oscillatory rheometry	-	- Enhanced efficiency with calcium incorporation - The effect over a time interval of up to 60 minutes was not impacted. - Lower effect compared with PC sample
[28]	Anhydrous Na- metasilicate	PCE (8 types)	Rotational rheometry	H-B*	6. Molecular weight, side chain length and side chain density are important to optimise the efficiency of PCE-based superplasticisers in AAS. 7. Molecule backbone charge type (i.e., anionic and cationic) do not significantly affect the superplasticiser efficiency
[80]	NaOH	MPEG PCE	Mini-slump and rotational rheometry	Not reported	8. Even in the same type of superplasticiser (i.e., MPEG PCE), significant variations can be observed depending on polymer architecture. 9. Acrylic acid monomers are more efficient than Methacrylic acid monomers to synthesise PCE superplasticisers for AAS. 10. AA-PCE resulted in lower values of viscosity and yield stress, indicating a better efficiency according to the rheometry measurement.

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*H-B = Herschel-Bulkley model; V** = Vinyl copolymer

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5.2. Metakaolin-based systems

992

993 In AAMKs, some authors consider the positive effect of commercial superplasticisers
 994 improving fluidity very low [41,90]. The reduced efficiency of superplasticisers in MK systems
 995 is well-known in Portland cement research. This is mainly attributed to physical and chemical

characteristics, such as this lamellar structure, high specific surface area and fineness, increasing the water and superplasticisers' necessity to adjust the rheological behaviour [92].

The influence of superplasticiser addition (not specified in the paper) on the workability of NaOH-activated MK systems was evaluated by Pacheco-Torgal et al. [93]. The study investigated the incorporation of superplasticiser at varying dosages from 0 to 3 wt.%, and the workability was assessed through mini-slump tests. The findings indicated that superplasticiser performance was generally superior at lower NaOH concentrations, suggesting that higher sodium content (i.e., %Na₂O) may impair the effectiveness of the superplasticiser. Specifically, the positive impact of the superplasticiser on mortar workability was more pronounced at lower dosages with reduced NaOH concentrations. As the alkali dosage increased, the beneficial effect of the superplasticiser was observed only at dosages exceeding 2 wt.%. Additionally, a nearly linear relationship was noted between superplasticiser content and mini-slump spread in samples with lower alkali dosage (10M NaOH). Furthermore, the authors proposed the inclusion of calcium hydroxide as a co-precursor, replacing MK in quantities up to 15 wt.%. As discussed, the addition of calcium enhances the action of the superplasticiser and improves particle dispersion due to the increased presence of divalent cations (i.e., Ca²⁺ ions), which favour the positive charging of MK particles [67].

Different from what was observed for AAS systems, the influence of superplasticisers on the rheological properties of MK-based AAMs remains inadequately explored. While some preliminary analyses have been conducted using mini-slump tests, the lack of comprehensive results (e.g., rotational and oscillatory rheometry measurements) highlights a significant knowledge gap regarding the application of superplasticisers in AAMs. Given that MK-based systems are among the most promising AAMs for future use, investigating this topic is of paramount importance. Therefore, a more comprehensive evaluation of different classes of superplasticisers, such as LS, PCEs, and NPs, is essential to advance understanding in this field. Current studies often present limitations both in the diversity of admixtures investigated and in the depth of analysis and discussion regarding their performance in AAMK binders.

5.3. Fly ash-based systems

The effect of different superplasticisers (LS, NP, M, PCE) and alkali dosage on the rheological behaviour of alkali-activated fly ash (AAFA) mixtures was investigated in a study by Zhang et al. [70], which provided valuable insights into the mechanisms influencing these systems. The

study highlighted that the NaOH concentration, when reaching 10 M, has a detrimental effect on the efficiency of various superplasticisers, as it reduces the absolute zeta potential. The authors suggested that the high alkalinity disrupts the structure of superplasticisers, breaking them down into smaller molecular fragments, which diminishes their performance in AAFA ash systems. Notably, NP-based superplasticisers exhibited the best performance under these challenging conditions. Similar findings were reported by Yan et al. [94], who studied a AAFA system activated with calcium carbide residue and Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$). In their study, the introduction of NP-based superplasticisers at contents up to 0.8% increased the absolute value of the zeta potential of the binders, further supporting the effectiveness of NP-based superplasticisers

In a comparison between NP and M-based superplasticisers, Li et al. [95] also obtained results indicating that NP-based superplasticisers are a good option to enhance the workability of AAFA, with mini-slump tests showing both higher performance and better flow maintenance compared to M-based superplasticisers. The rapid performance loss of M-based superplasticisers is attributed to the decomposition of triazine rings into ammonia and carbon dioxide, according to the authors. On the other hand, a comparison between PCE, NP and M-based superplasticisers was conducted by Alrefaei et al. [57], where the authors observed the best dispersion ability and increased workability from the PCE-based superplasticisers in a one-part AAFA binder activated by $\text{Ca}(\text{OH})_2$ and Na_2SO_4 .

Despite these findings, there is no consensus on the most promising superplasticiser (in terms of dispersion ability) to use in AAFA and on the mechanisms by which these admixtures act. Similar to what was mentioned in the previous sections of GGBFS and MK, the most crucial factors impacting superplasticiser performance appear to be related to the presence of calcium and activation parameters (e.g., alkali dosage, silica modulus, type of activators), rather than being directly linked to the precursor used, although this parameter remains important. Rheological studies focusing on AAFA systems incorporating superplasticisers remain a gap in the literature, with most existing research limited to binary or ternary systems in which FA is not the primary precursor.

6. Practical implications. Limitations, and pathways

Despite notable progress, significant challenges remain in the use of admixtures for AAMs. As discussed, conventional superplasticisers often show reduced efficiency in highly alkaline and ion-rich environments, requiring higher dosages than usual for PC systems to achieve adequate dispersion. While superplasticisers are typically used at 0.3–1%wt. of PC, in AAMs, the required dosage would exceed 1% for the same workability, which directly increases material costs and hinders scalability. Even at higher dosages, conventional admixtures may still perform poorly due to factors such as alkalinity, ionic strength, and the complex chemistry of AAM systems, which highlights the need for further research in this field.

Beyond dosage, the availability and cost of raw materials used in the synthesis of advanced admixtures represent another barrier. According to Lei, Hirata, and Plank [21] some macromonomers are more accessible and established in the market, such as MPEG- and IPEG. Macromonomers such as EPEG, GPEG, IPEG, or APEG are expensive or difficult to obtain, while certain polymers are not even commercially available. Additionally, synthesis processes often require high-cost equipment, further restricting large-scale adoption.

At the same time, new trends are moving towards the design of novel or modified polymers, with PCEs offering particular promise due to their versatility and efficiency at low dosages. However, to fully realise their potential, investment is needed in developing more sustainable and cost-effective synthesis processes. This will require collaboration between academia and industry, as well as the exploration of innovative tools. Approaches such as artificial intelligence, dynamic modelling, and nano-scale testing are increasingly being applied to understand admixture–precursor interactions, especially with increased use of novel SCMs. These tools can provide new insights, optimise formulations, and ultimately accelerate the

development of next-generation admixtures tailored for complex systems such as AAMs or other low-carbon cements.

7. Conclusions and key knowledge gaps

This review has consolidated current and foundational knowledge regarding the dispersion mechanisms of superplasticiser admixtures in AAMs, drawing from both recent and classic publications. Based on the findings presented in this review, the following key conclusions and knowledge gaps can be drawn:

- Most studies on superplasticisers in AAMs focus on slag and fly ash, with limited research on MK-based systems.
- Among superplasticiser types used in AAMs, PCEs are the most common, followed by NP-, LS-, and M-based admixtures. Novel and modified PCE-based superplasticisers are a growing topic of research. More nano and atomic research may help this field.
- Rheometry, though valuable for analysing AAM rheology across various shear rates, remains underused in assessing superplasticiser performance. Combined with techniques like zeta potential, it offers deeper insights. Modified Bingham and Herschel-Bulkley models have a better fit.
- Despite extensive PCE use in AAMs, the impact of their molecular structure is not systematically understood due to limited supplier data and great variability of results depending on the characteristics of the materials and mixtures;
- Recent studies describe that the high pH and ionic strength in pore solution, along with shifts in surface particle zeta potential, impair superplasticiser performance due to solubility issues, partial degradation, and consequent polymer agglomeration.
- Future investigations into the rheology of AAMs with superplasticisers should focus on the agglomeration and flocculation phenomena induced by high ionic strength and high-pH environments. A better understanding of these microstructural mechanisms will be essential for guiding the design and development of next-generation superplasticiser admixtures tailored for these complex, low-carbon systems.
- Electrostatic repulsion and steric hindrance are the mechanisms driving the particle surface interactions between superplasticisers and cement particles. Cations such as Ca^{2+} can facilitate superplasticisers' adsorption due to the alteration in the EDL.

- Future research should explore mechanisms affecting superplasticiser performance, including PCE with varied motif structures, novel formulations, and especially one-part and MK-based AAMs, which are currently underexplored.
- Based on PCE in AAS, a molecular structure of high Mw ($\geq 90,000$ Da), high anionicity (≥ 7), and short side chain length ($N_{EO} = 7$) is indicated for most macromonomers. The type of acids and structural motifs also influences PCE performance. However, the performance may change depending on the activator and precursor used.

Acknowledgements

The participation of MRCS was sponsored by a PhD scholarship (Studentship 2735216) from the Engineering and Physical Sciences Research Council (EPSRC), UK, administered through the Energy Institute, The University of Sheffield. CNPq sponsored APK through the research fellowship 311893/2021-0. ICC acknowledges the financial support from the Coordination for the Improvement of Higher Education Personnel (CAPES), Brazil. LS acknowledges the financial support from CNPq and Fundação Araucária.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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