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# Future perspectives for alkali-activated materials: from existing standards to structural applications

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#### Abstract

The production of cement and concrete contributes significantly to global greenhouse gas emissions. Alkali-activated concretes (AACs) are a family of existing alternative construction materials that could reduce the current environmental impact of Portland cement (PC) production and utilisation. Successful applications of AACs can be found in Europe and the former USSR since the 1950s and more recently in Australia, China and North America, proving their potential as construction materials. However, their utilisation is limited presently by the lack of normative and construction guidelines. Raw materials' non-uniform global availability and variable intrinsic properties, coupled with the lack of specific testing methods, raise questions regarding reproducibility and reliability. The mechanical and chemical behaviour of AACs has been investigated extensively over the past decades, strengthening its potential as a sustainable substitute for traditional PC-based concrete. Although a wide amount of studies demonstrated that AACs could meet and even exceed the performance requirements provided by European design standards, a classification of these broad spectra of materials, as well as new analytical models linking the chemistry of the system components to the mechanical behaviour of the material, still need further development. This report gives an overview of the potential of alkali-activated systems technology, focusing on the limitations and challenges still hindering their standardisation and wider application in the construction field.

Keywords: Alkali-activated concrete; Mechanical performance; Real-scale applications; Performance-based standards; Sustainable construction

#### 1 Introduction

Portland cement (PC) production is acknowledged as one of the major causes of global anthropogenic CO<sub>2</sub> emissions due to the combustion of fossil fuels and the decarbonation of limestone during the high-energy-demanding production process [1]. As the demand for construction materials drives cement and concrete production, minimising emissions while supplying enough material to meet increasing demand will be challenging. To achieve the carbon neutrality proposed by the European Green Deal by 2050, the cement industry needs to act at every stage of the value chain to meet net-zero emissions by 2050 [2]. Reducing the clinker-to-binder ratio via partially replacing PC with supplementary cementitious materials (SCMs) represents a valid solution to achieve significant emission savings from cement production. However, among the available solutions to limit cement and concrete environmental impact [3], alkali-activated concretes (AACs) are a promising class of clinker-free binders able to convert a significant number of industrial by-products and

wastes into construction materials, reducing emissions and energy consumption related to cement production [4,5].

The continuous progress in understanding AACs' reaction mechanisms and mechanical and durability performance, supported by a long history of successful applications, demonstrate that AACs can perform similarly or even better than traditional Portland cement-based concrete (PCC) as construction materials [6]. The wide range of solid precursors and alkali-activators suitable for alkali-activated concrete makes them extremely variable, allowing fit-for-purpose mix design formulations to achieve the mechanical and durability performance required by the end applications. However, each mix design formulation differs from the others in terms of the chemical composition of both precursors and alkaline solutions. Thus, the reaction mechanisms taking place in the different mix design formulations need to be further investigated and linked to the concrete mechanical and durability performance. The potential of AACs as a versatile building material is hindered by the lack of analytical

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equations and models correlating the chemistry of the reaction with the material performance, which represent the core of design regulations and standards. Current prescriptive design standards developed for Portland cement concrete need to be modified and further implemented for AACs to reflect the novelty of the material characteristics and facilitate their use in structural and non-structural applications. In addition to the lack of correlations between AACs chemistry and performance, durability data obtained from natural conditions are limited. This is mainly due to the lack of design regulations limiting the use of AACs in real-scale applications. Only a limited number of pilot-scale works have been realised in recent years, allowing monitoring of the material behaviour over its service life. Additionally, new reliable and adequate testing methods [7] to evaluate the long-term performance of AACs at a laboratory scale need to be implemented.

The purpose of this paper is to draw attention to the versatility of AAC as an alternative to traditional concrete, while also raising awareness of the barriers and limitations preventing their widespread commercialisation and use in the construction industry. A current picture of the AAC technology path, from laboratory research topic to market available product, is given to underline the general challenges related to the high chemical variability of the material components. From an analysis of available mix design components and formulations, through an overview of worldwide real-scale applications, to the need for new performance-based standards and analytical correlations between chemistry and performance, it is clear that changes in research, industry and building regulations need to be made. Therefore, the primary goal of this study is to assess the material's short-term mechanical performance, which is urgently required to develop standardised design codes for alkali-activated concrete structural applications. Understanding the material's long-term behaviour and the durability of reinforced structures, especially the performance development over time, represent another crucial challenge for the utilisation of this novel material in the construction industry, which cannot be neglected. However, as the durability of alkali-activated concrete has been investigated thoroughly in previous studies [7], it is not further discussed in this work.

In the current study, only ground granulated blast furnace slag (GGBFS), fly ashes (FA) and blended systems (GGBFS + FA), activated by sodium hydroxide (SH), sodium silicate (SS), or a combination of them, are considered. Due to the high number of data available in the literature for these types of alkali-activated binders, they have been chosen to evaluate the efficacy of current analytical models to predict the mechanical performance of high-calcium (GGBFS) and lowcalcium (FA) alkali-activated systems according to the chemistry of their components. Several other existing aluminosilicate sources have been evaluated in recent years as novel precursors for alkali-activated concrete, to which the considerations made from here on can be applied. Depending on their chemical composition and amorphous content, they can undergo an activation process in which reaction mechanisms can be comparable to the ones shown by the

most common GGBFS or FA. Additionally, activator types and mix design formulations can be varied and optimised to meet specific application performance demands.

#### 2 Mix design challenges of AACs

Alkali-activated concrete, like traditional PCC, is obtained by different proportions of binder, liquid, and (fine and coarse) aggregates. However, if for PCC, binder and liquid are generally mainly cement and water, for AAC, a variety of solid precursors and chemical activators, in liquid or solid forms [8–11] are suitable for alkali-activation (Table 1).

Table 1. Main components used for the production of PCC and AAC.

Component	PCC	AAC
Binder	Cement (CEM I – CEM V) Supplementary cementitious materials (SCMs) as cement replacement	By-products of foundries and metal production plants (ferrous slags, i.e. blast furnace slags, ladle slags, electric arc furnace slags, non-ferrous slags, i.e. copper slags) By-products of combustion processes (coal fly ashes, coal bottom ashes, rice husk ashes, sugar cane bagasse ashes, palm oil fuel ashes) By-products of bauxite refining (red mud) Municipal solid wastes incineration (MSWI) ashes Mineral extraction wastes Calcined clays
Liquid	Water	Alkaline solution (alkalis and/or soluble silica sources and/or water)
Aggregates	Fine and coarse aggregates (sand and gravel)	Fine and coarse aggregates (sand and gravel)
Admixtures	Chemical/mineral admixtures	Chemical/mineral admixtures(*)

(\*) Many of the chemical admixtures developed for PCC become much less effective in AAC due to the structural instability and complex interactions in the alkaline media [12].

To be suitable for the alkali-activation process, the material chosen as binder needs to contain reactive aluminosilicates, with a certain degree of amorphous content, in combination with calcium oxide (CaO), in which the amount of the latter generally defines the classification of AACs in high-calcium (CaO content > 10 wt%) and low-calcium (CaO content < 10 wt%) systems [13], [14]. Considering these requirements, a vast list of materials presents sufficient reactivity potential to be used as a binder alone or in combination with others in blended systems, as shown in Table 1. The possibility of reusing by-products from different industrial sectors is one of the main environmental advantages of AACs production [15–22]. However, the by-product nature of the binder involves a wide range of chemical and mineralogical variability, influenced by the location of the raw material source and the

primary industrial processes from which they are derived [23,24].

Among the possible binders reported in Table 1, ground granulated blast furnace slags (GGBFS) and calcareous fly ashes (name also class C fly ashes - FA-C), and siliceous fly ashes (named also class F fly ashes (FA-F)) have been chosen as representatives of high- and low-calcium alkali-activated systems, respectively, due to a larger number of studies on reaction mechanism and related products and performance. High- and low-calcium systems require different activation conditions, mainly dependent on the chemical composition and the binder amorphous phase content, besides other factors such as particle size or specific surface area, which are not considered in this study. Due to its high calcium content (CaO > 10 wt%) and its amorphous nature, GGBFS and FA-C require mild alkaline conditions for the reaction process [25], the main product of which is calcium (aluminium) silicate hydrate gels (C-(A)-S-H) [26,27]. On the other hand, FA-F shows lower latent hydraulic potential (CaO < 10 wt %) and/or higher amount of crystalline phases compared to high-Ca binders, resulting in the need for stronger alkaline solutions or heat curing [28–31] to promote the reaction mechanism and the formation of sodium aluminosilicate hydrate gels (N-A-S-H) [32,33].

The differences in the initial mineralogy and chemistry of the precursors, combined with the different alkaline activators dosages and compositions suitable to promote the reaction, introduce several new critical factors in the mix design formulation, affecting the fresh and hardened concrete properties [34,35]. Therefore, it is fundamental to understand how these chemistry-linked parameters influence the concrete behaviour, in particular compressive strength, to which all the material mechanical properties are correlated in standards and design regulations. Table 2 collects the influential factors for AAC mixtures, and how they compare to those conventionally considered for PCC mixes. The difficulties in the definition of a general mix design procedure and, consequently, in the use of formulation parameters to correlate the chemistry of the mix components with the concrete performance, represent the most challenging obstacle for the standardisation of AACs [33,35-37]. In addition, a fine analysis of a specific precursor regarding the reactive and less/non reactive components is critical and necessary for both successful choice and proper formulation of AACs [36].

Table 2. Main parameters involved in the mix design formulation of OPC and AACs

OPCC	AAC
	Precursor type
	Amorphous degree
Cement type	Reactivity index
	CaO/SiO <sub>2</sub> ratio
	CaO, MgO, Al <sub>2</sub> O <sub>3</sub> content
Minimum comont contant	Minimum precursor(s) content
	Na₂O/binder ratio
	Optimised choice of activator
Water content	Activator type
Water content	SiO <sub>2</sub> /Na <sub>2</sub> O ratio (Ms)
water/cement (w/c) ratio	Water/binder (w/b) ratio
	Liquid/binder (I/b) ratio
Aggregates	Aggregates
Curing parameters	Curing parameters

Unlike PCC, whose compressive strength is negatively affected by the water-to-cement ratio (w/c) [38,39], for AAC, it is difficult to establish a single parameter directly affecting the compressive strength, as multiple factors interact to influence its value and development in time. Furthermore, the water-to-cement ratio used for PCC cannot be translated into a water-to-binder ratio (w/b) for AAC, as the liquid involved in the reaction is not just water but also a combination of alkalis and/or soluble silica sources and/or extra water. Three different forms of liquid-to-binder ratios can be defined for AAC, all affecting the material performance differently. The total liquid-to-binder ratio (I/b) considers all the liquids in the mixture as a whole; the water-to-binder ratio (w/b) takes into account the amount of water included in the alkaline activators and the extra water added to the mixture; and the total alkaline activators-to-binder ratio (a/b), only includes the alkaline components of the solution. Although the total I/b and the w/b do not show a clear correlation with the compressive strength, mechanical performance can be roughly linked to the total alkaline activators-to-binder ratio (for a given total I/b and constant water content) [35].

Table 3 shows the main parameters of the alkaline solutions, i.e. the alkali concentration *n*, defined as the number of alkalis for 100g of binder [wt%], and the silicate modulus  $M_s$ , i.e. the molar ratio between SiO<sub>2</sub> and Na<sub>2</sub>O, and their optimal dosage for low- and high-calcium systems. The alkali content and the silica modulus, in combination with the binder characteristics, govern the chemistry of the mix design formulation and thus the reaction mechanisms, directly affecting the mechanical properties of the material [40,41]. Due to the countless possible binders-activators combinations, it is difficult to generalise the effect of the system chemistry on the mechanical performance. For this reason, it is necessary to find and highlight recurring behaviours and correlations between chemistry and mechanical performance.

 Table 3. Main characteristics of the alkaline solutions used for AAC production [13].

	Alkaline potential of the solution	Dosage of M <sub>2</sub> O*(n)	Ms= SiO2/M2O
Low-calcium systems (CaO content < 10 wt%)	High	7.0 – 9.0 wt%	1.0 - 2.0
High-calcium systems (CaO content > 10 wt%)	Low	3.0 – 6.0 wt%	~ 0.75

(\*) M stand for the specific cation, usually K or Na [13]

#### 3 Real-scale applications

Although the recent increasing demand for greener alternatives to traditional concrete has prompted further research and investigations into AAC, this technology and its application in construction projects are not new. The development of AAC has been undertaken in the post-World War II era, with the first applications in the 1950s [42,43] when a blast-furnace slag-based concrete activated with only

Table 4. Examples of real-scale applications of AACs.

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calcium hydroxide or in combination with sodium sulfate, named "Purdocement", was first used in Belgium for the realisation of several buildings [43]. Since then, numerous structures have been realised, including civil waterworks, pavements, roads, conventional pre-cast products and, most recently, large-scale cast-in-situ projects (Table 4).

Despite these construction works demonstrating over 60 years of service life and their durability outside of laboratory conditions, the commercialisation of AACs did not arise until the highly considerable carbon emissions from conventional OPC manufacture became a concern. This resulted in a worldwide research campaign to better understand and characterise these new construction materials, favouring the drafting of dedicated design guidelines and specifications, which promoted their commercialisation and practical utilisation, as documented first in Australia, and recently in the United Kingdom. Table 5 lists a selection of recently commercialised alkali-activated materials whose successful utilisation in several on-site trials and projects further confirms their potential as construction materials and as traditional concrete alternatives.

Year	Location	Construction work	Material	Ref.
1952- 1959	Brussels, Belgium	Parking 58	Purdocement (GGBFS + PC activated by $Ca(OH)_2 \text{ or } Na_2SO_4)$	[43]
1960- 1980	Mariupol, Ukraine	2-storey and 15-storey residential buildings	Alkali-hydroxide activated GGBFS concrete	[42]
1966	Odessa, Ukraine	Drainage collector No. 5	Alkali-carbonate activated GGBFS concrete	[42]
1974	Krakow, Poland	Storehouse	Precast steel-reinforced alkali-carbonate activated GGBFS concrete	[42]
1986- 1994	Lipetsk, Russia	24-storey residential building	Alkali-carbonate activated GGBFS concrete	[42]
1988	Yinshan County, Hubei Province, P.R. China	6-storey office and retail building	Sodium sulfate-activated Portland-slag cement concrete	[42]
2009	Melbourne, Australia	Salmon St Bridge	E-Crete precast footpath panel segments (180 precast footway units)	[44]
2009	Brisbane, Australia	Murrarie Plant site bridge	EFC precast bridge decks	[45]
2010	Melbourne, Australia	Thomastown Recreation and Aquatic Center	E-Crete footpaths and driveways	[44]
2012	Melbourne, Australia	Melton Library	E-Crete precast panels and in-situ works	[44]
2013	Queensland, Australia	Global Change Institute (GCI) Building, University of Queensland	EFC – 33 precast floor beam-slab elements	[45]
2013	Irvine, California, USA	Sustainable concrete solar- powered house	Precast alkali-activated fly ash concrete members	[46]
2013	Yuozhong District, Chongqing, P.R. China	Chongqing Research Institute of Construction Science office building	Cast in-situ alkali-activated GGBFS concrete	[47]
2014	Toowoomba, Australia	Toowoomba Wellcamp Airport	EFC – cast in-situ heavy-duty pavements	[45]
2017	London, UK	Thames Tideway Central, Kirtling Street	Cemfree – cast in-situ	[48]
2020	Wageningen, Netherlands	Cycle bridge	RAMAC (prefab)	[49]
2021	Chatham, UK	Chatham railway station (step-free access foundation)	Cemfree – 300 m <sup>3</sup> cast in-situ	[48]
2021	Le Havre, FRA	Grand Port Maritime du Havre	Exegy – concrete barrette (17 m depth)	[50]

Product name	Company	Composition	Ref
E-Crete <sup>™</sup>	Zeobond Pty Ldt (Australia)	Fly ash and slag	[44]
EFC (Earth Friendly Concrete)	Wagners (Australia)	Blast furnace slag and fly ash chemically activated	[45]
Cemfree	DB Group (UK)	GGBFS and pulverised fuel ash (PFA)	[48]
Vertua <sup>®</sup> Ultra	CEMEX (UK)	Geopolymer clinker-free concrete	[51]
Blockwalls™	Virtus Concrete Solutions Ltd (UK)	Pre-cast geopolymer concrete blocks made from reclaimed stone, kiln ash, inert waste and sodium silicate sourced from recycled e-waste	[52]
RAMAC	SQAPE BV (NL)	Ready-mix cement-free concrete	[49]
Exegy	Soletanche Bachy (FRA)	GGBFS activated with sodium carbonate	[50]

Table 5. Examples of recently commercialised alkali-activated materials

## 4 Towards performance-based standards for AACs

The increasing number of successful applications of AACs in construction encouraged research institutes and construction industries to further investigate material behaviour and develop new approaches to broaden its use. However, since the positive impact of these alternative binders is coupled with several limitations, research efforts often encounter the resistance of regulatory bodies, due to the not yet overcome challenges in linking chemistry and structural performance, and the limited number of adequate durability data, hindering the standardisation process of alkali-activated concrete technology.

To promote the use of AACs as an alternative to traditional cement-based concrete, avoiding the timeframe required to draft national or international standards, performance-based design specifications represent the most feasible solution [4,53], as firstly demonstrated in Australia and most recently in the United Kingdom. This approach led in 2011 to the development of the "Concrete Institute of Australia (CIA) Recommended Practice for Geopolymer Concrete", a practical guideline defining the mechanical behaviour and the short- and long-term properties of geopolymer concrete, providing design equations and methods for its application in the construction field. In the following years, Austroads, the peak organisation of Australasian road transport and traffic agencies, developed additional specifications [54,55] for the use of geopolymer concrete in the manufacture of structural and non-structural components, promoting their utilisation in several infrastructural projects, as described in the previous section. In the same years, in the UK, the British Standards Institute Publicly Available Specification (PAS) 8820:2016 "Construction materials - alkali-activated cementitious material and concrete - Specification" represented the first attempt in Europe to develop performance-based design guidelines for the adoption of AACs in the construction industry. This guideline specifies a means of assessing the performance and durability requirements for alkali-activated concretes to facilitate and encourage their use in construction projects. The PAS 8820:2016 sets the maximum possible Portland cement content at 5% mass of binder solids and provides recommendations about concrete mixing, placement, curing and testing. In the PAS 8820:2016, the chosen alkali-activated material-based binder needs to be tested in parallel with a reference cement-based concrete and is required to achieve at least equivalent or superior

mechanical and durability performance requirements defined in the BS 8500, the British standard for PCC. Existing standardised testing methods for traditional concrete are analysed and implemented, if needed, with modifications targeted at the performance of AACs. The choice to undergo the PAS process instead of the standardisation process allowed the rapid development of a specification to fulfil an immediate need in the construction industry.

For instance, the proposition of a performance-based approach for standards and design codes of a new technology requires a high degree of confidence level. Hence, it is necessary to demonstrate the safety and reliability of AACs as construction materials, and their ability to meet mechanical and durability performance requirements. The RILEM Technical Committee 247-DTA has performed round-robin testing programs to assess the reproducibility of the mechanical behaviour of different binders and their durability performance [17,56,57]. The investigations demonstrated how the variability and the complexity of the mix design formulation can lead to different results, mainly in durability parameters, even following the same mixing and testing procedures. For this reason, it is fundamental to evaluate separately the performance of AACs according to binder type and mix design proportions, which affects the hardened material behaviour. Blast furnace slags, for example, show higher intrinsic reactivity, and therefore require milder activating conditions [27,58], although it is followed by significant autogenous shrinkage levels [59-61] and potential carbonation [62]. On the other hand, fly ash requires activation-enhancing practices, such as heat curing and higher alkalinity [27,63], which, if not properly controlled, results in flash setting [56,64] and coarser microstructure, leading to issues related to the transport of undesired species [57]. Moreover, other novel precursors, the majority of which are summarised in Table 1, could deliver interesting punctual characteristics [17,65-68] and, while not sufficient to be utilised as sole precursors, could be used as part of mixtures with other components aiming to specific performance.

It is indeed necessary to classify alkali-activated concretes in classes according to the characteristic of the main constituents, analysing each class separately and developing targeted standards based on laboratory experiments data regarding both mechanical and durability performance.

#### 5 Analytical correlations of mechanical properties of AACs

The assessment of the mechanical performance of alkaliactivated concrete through laboratory testing and the evaluation of the effect of the chemistry of the mixture formulation on the material behaviour are essential for the production and classification of AACs. In addition, the design of equations and empirical correlations between mechanical properties must be defined to facilitate their use as reliable structural materials. Code-based analytical equations developed for traditional cement-based concrete (Table 6) correlate the 28-day compressive strength, a relatively easy parameter to be determined experimentally, to the mechanical properties relevant to structural design, such as (direct or indirect) tensile strength and modulus of elasticity.

As direct comparisons with PCC are always the starting point of analysis, the same correlations are expected to be observed in the case of AACs. To verify the suitability of the analytical expressions proposed in Table 6 in predicting mechanical performance, literature data regarding the mechanical properties of different types of AACs have been collected and analysed [69-91]. The 28-day compressive strength of alkali-activated mixtures obtained with different binders (GGBFS, FA-F and FA-C, and blends of GGBFS and FA-F), activated with either sodium hydroxide or sodium silicate, was used to predict their modulus of elasticity  $(E_c)$  and the tensile strength ( $f_{ct}$ ) according to the correlations in Table 6. Equations using the concrete density as a parameter to estimate the modulus of elasticity have not been considered. Only literature providing fully detailed mix design formulations, including activator type and dosage (molarity of sodium hydroxide, silicate modulus, contents of components of sodium silicate), extra water content, aggregates (type and content) have been analysed [69-91]. The correlations use the characteristic cylindrical compressive strength and the tensile strength values obtained by performing splitting Eurocode 2.

Fig. 1 shows the correlations between the 28-day compressive strength and the 28-day modulus of elasticity (Fig. 1a) and tensile strength (Fig. 1b), and predictions of current code-based equations (Table 6). The two experimentally obtained properties present a direct correlation with each other, following the trends given by the design codes. It is possible to observe a largely scattered pattern of the total data points, which is decreased when each precursor is individually analysed. Although the correlation of properties of PCCs using the same code-based equations also presents dispersed data [92], Fig. 1 demonstrates that the vast majority of data points are located below the trendlines. The variable distance between reported and predicted values, according to the type of precursor, indicates that the current design codes fail to deliver a reliable and comprehensive prediction of the mechanical performance of all types of AACs. In general, a lower modulus of elasticity of alkali-activated concretes is expected compared to traditional cement-based concretes [60,74,75,93-95]. However, different precursors were observed to display different behaviours. Concrete mixes using siliceous fly ashes present values of  $E_c$ , in general, lower than calcareous fly ashes, with the latter displaying similar behaviour to slags. In the case of FA-F, curing conditions were observed to have a major influence on final properties. Heat curing, classified here as concrete mixes cured at temperatures above 50 °C for at least 24 h (FA-F HT), showed improved mechanical properties compared to ambient cured ones (FA-F RT). Blending FA-F with slag approximates the  $E_c$  to the correlations proposed by the model codes, although still overestimates it.

Table 6. Current analytical equations for PCC to predict tensile strength and modulus of elasticity from the compres	sive strength.
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Standard	Tensile ( $f_{ct}$ ), splitting tensile ( $f_{ct,sp}$ ), and flexural ( $f_{ct,fl}$ ) strength correlated to the 28-day compressive strength ( $f_{ck}$ )	Modulus of elasticity
Eurocode 2 (2021)	$f_{ctm} = 0.3 f_{ck}^{2/3}$ , $f_{ck} \le 50 MPa$	$E_{cm} = k_E f_{cm}^{1/3}$
fib Model Code 2010	$\begin{aligned} f_{ctm} &= 1.1_{f_{ck}} - , \ f_{ck} > 30 \ MPa \\ f_{ctm} &= 0.3 f_{ck}^{2/3} , \ f_{ck} \le 50 \ MPa \\ f_{ctm} &= 2.12 \ln \left( 1 + 0.1 (f_{ck} + \Delta_f) \right), \ f_{ck} > 50 \ MPa \\ f_{ctm} &= f_{ctm,sp} \\ f_{ctm} &= \alpha_{fl} f_{ctm,fl}, \ \alpha_{fl} = \frac{0.06 h_b^{0.7}}{1+0.06 h_b^{0.7}} \end{aligned}$	$E_{ci} = E_{c0} \alpha_E \left(\frac{f_{ck} + \Delta_f}{10}\right)^{1/3}$
AS3600 (2009)	$f_{ctk} = 0.36\sqrt{f_{ck}}$ $f_{ctk,fl} = 0.60\sqrt{f_{ck}}$	$E_{cj} = 0.043 \rho^{1.5} \sqrt{f_{cmi}}, f_{cmi} \le 40 MPa$ $E_{cj} = 0.024 \rho^{1.5} (\sqrt{f_{cmi}}) + 12, f_{cmi} > 40 MPa$
ACI-363 (2010)	$f_{ct,sp} = 0.59 \sqrt{f'_c}$ $f_{ct,fl} = 0.94 \sqrt{f'_c}$	$E_c = 3320\sqrt{f'_c} + 6900$
ACI-318 (2011)	$f_{ct,sp} = 0.56\sqrt{f'_c}$ $f_{ct,fl} = 0.62\sqrt{f'_c}$	$E_c = 33\rho^{1.5}\sqrt{f'_c}$

a 70

60





28-day compressive strength (MPa)

Figure 1. Correlations between compressive strength of AACs and (a) modulus of elasticity; (b) tensile strength (see Appendix for more details about the collected datapoints).

Also for the 28-day tensile strength, different behaviours according to the binder type can be noticed. High-Ca precursors tend to display higher values of tensile strength, with predictions underestimating their properties above a threshold compressive strength of 30 MPa. In the case of FA-C, the majority of the analysed data displays a strong correlation with code-based equations up to compressive strength values of 60 MPa. On the other hand, for mixtures of FA-F solely or blended with slag, code-based equations significantly overestimate their behaviour, with most data points located far below the model codes for compressive strength above 30 MPa. Below this threshold, FA-F still presents a good correlation.

Overestimation and underestimation of mechanical properties could represent significant problems for the design of concrete structures, with a direct impact on their fabrication process, nature of application, performance and service life. The elastic modulus is crucial for the understanding of concrete deformations, mainly caused by creep and load relaxation, and directly affects the long-term behaviour of the structure. Consequently, both overestimation and underestimation of  $E_c$  observed for AACs, come with concern and can affect the safety level of structural elements, and this elucidates that deformation mechanisms must be fully understood in these alternative structural materials. The overestimation of the tensile strength represents a non-negligible issue, as it can compromise the integrity of the entire structure, causing unexpected failure if higher values of maximum permissible loads are assumed. Therefore, the correlation of mechanical properties for the prediction of tensile strength should be subject to a conservative approach, which is not observed when PCC-based equations are used to estimate the performance of AAC.

Overestimation and underestimation of the 28-day mechanical properties could represent significant problems for the design of concrete structures, with a direct impact on their fabrication process, nature of application, performance and service life. The elastic modulus is crucial for the understanding of concrete deformations, mainly caused by creep and load relaxation, and directly affects the long-term behaviour of the structure. Consequently, both overestimation and underestimation of  $E_c$  observed for AACs, come with concern and can affect the safety level of

structural elements, and this elucidates that deformation mechanisms must be fully understood in these alternative structural materials. The overestimation of the tensile strength represents a non-negligible issue, as it can compromise the integrity of the entire structure, causing unexpected failure if higher values of maximum permissible loads are assumed. Therefore, the correlation of mechanical properties for the prediction of tensile strength should be subject to a conservative approach, which is not observed when PCC-based equations are used to estimate the performance of AAC.

Although AACs differ from traditional concrete in terms of reaction mechanism and reaction products, the analytical expressions developed for PCC are more suitable to describe the behaviour of slag- and calcareous fly ash-based concretes, which can be explained partially by the nature of obtained reaction products. The primary phase formed for high-Ca binders is a C-A-S-H gel [96,97], chemically and structurally similar to C-S-H gels formed in PCC mixtures. Oppositely, low-Ca systems have N-A-S-H gels as the main reaction product [27,98], a phase with a strong tendency to form a cementitious matrix more cohesive than other gels, resulting in a more brittle microstructure and lower tensile strength compared to high-calcium systems [77,99] of the same strength class (> 60 MPa).

Current code-based models generally underestimate the tensile strength [35] and significantly overestimate the modulus of elasticity of AACs, as shown in Fig. 1. Following this discrepancy, recent studies investigated their mechanical properties and proposed new constitutive models to predict their performance behaviour more accurately (Table 7).

Fig. 2 shows the ability of the equations in Table 7 in predicting the mechanical performance of alkali-activated concretes. In general, the proposed correlations approximate the experimental behaviour of AACs to predicted values. However, although similar trends are observed for the estimated values, a higher variation degree between equations is noticed in Fig. 2a. This variation is even clearer for tensile strength (Fig. 2b), as the ultimate calculated values vary from 10.2 MPa (Thomas and Peethamparan [74]) to 3.84 MPa (Lee and Lee [95]) for a compressive strength value of 90 MPa.

 Table 7. Current constitutive models developed for AACs.

Table 7. Current constitutive mode	is developed for AACS.	
Authors	Tensile ( $f_{ct}$ ), splitting tensile ( $f_{ct,sp}$ ), and flexural ( $f_{ct,fl}$ ) strength correlated to the 28-day compressive strength ( $f'_c$ )	Modulus of elasticity [MPa]
Yang et al. (2012) [100]	$f_{ct} = 0.255 (f'_c)^{0.65}$	$E_c = 4600 \left(\frac{\rho_c}{2200}\right)^{1.5} \sqrt{f'_c}$
Lee and Lee (2013) [95]	$f_{ctm,sp} = 0.45 \sqrt{f'_c}$	$E_c = 5300 (f'_c)^{1/3}$
Thomas and Peethamparan (2015) [74]	$f_{ct,sp} = \frac{2}{5} (f'_{c})^{\frac{7}{9}}$ $f_{ct,sp} = 1.08 \sqrt{f'_{c}}$	$E_{c} = 2900 (f'_{c})^{\frac{3}{5}}$ $E_{c} = 4400 \sqrt{f'_{c}}$
Xie et al. (2020) [35]	$f_{ct,fl} = 0.55 (f'_c)^{0.6}$ $f_{ct,sp} = 0.35 (f'_c)^{0.65}$	$E_c = 3650 \sqrt{f'_c}$
Cui et al. (2020) [101]	$f_{ct} = 0.0876 f'_{c} + 0.0585$	$E_c = 874.5(f'_c)^{0.85}$



Figure 2. Correlations between compressive strength of AACs and (a) modulus of elasticity; (b) tensile strength (see Appendinx).

Despite the proposition of several equations in the last decade, each one of them focused on the analysis of a limited amount of data obtained from the available literature or experimental investigations. Thomas and Peethamparam [74] focused their work on the alkali-activation of high-Ca binders, using slag and calcareous fly ash as binders. Lee and Lee [95] dedicated their work to blends of siliceous fly ash and slags, with the former being the main component of the mixture (> 80 wt%), Yang et al. [100] worked with slag-based concrete activated with calcium hydroxide. Cui et al. [101] based the proposed equations on high temperature cured siliceous fly ash based concrete, while Xie et al. [35] derived equations based on a wide range of precursors, considering both traditional (slag and siliceous fly ash) and alternative ones (biomass waste ashes).

In general, the slope of the curves of the proposed equations in Fig. 2a is noticeably lower than in Fig. 1a. If individual precursors are considered, the prediction of the modulus of elasticity is more closely related to experimental values, indicating a lower degree of overestimation of this property. Equations proposed by Yang et al. [100] and Thomas and Peethamparam [74] reach the highest values of  $E_c$ , following the known behaviour of slag-based concretes. The work from Cui et al. [101] and Lee and Lee [95] present an overall good agreement with experimental data of mixtures containing FA-F individually and in blends with slag. An underestimation of the performance of room temperature cured siliceous fly ash by all equations represents the need for a deep understanding of the mechanisms of microstructure evolution of this class of binders.

Differences between derived equations available in the literature are inevitable, as the broad spectrum of available AACs implies many variabilities to be considered. A more significant influence of precursors and their obtainment route is observed in Fig. 2b. While the works from Yang et al. [100] and Lee and Lee [95] are in agreement with the referred precursors, equations proposed by Cui et al. [101] and Thomas and Peethamparam [74] are observed to be outliers in the chart. In both cases, part of the concrete mixtures designed by the authors was subject to high-temperature curing (80 °C and 55 °C, respectively). While heat-curing of slag and calcareous fly ash binders is known to significantly affect their tensile strength [29][102][103], all of the data points acquired in the present work for high-Ca based concrete mixtures represent room temperature curing processes. Consequently, an overestimation of the mechanical performance is perceived from the trendline proposed by Thomas and Peethamparam [74], although BFSbased concrete presents the highest values of tensile strength among all mixtures analysed. As for Cui et al. [101], the linear trendline presents increasing disagreement with collected data regarding the evolution of compressive strength. It can thus be assumed that high-strength AACs require a different approach for the correlation of properties, and the use of linear equations for the prediction of performance, even for the same class of concrete, should be avoided.

As visualized in both charts in Fig. 2, the equations proposed by Xie et al. [35] present a rough average of the other four.

The visualization of such behaviour is expected since the author considered both high- and low-Ca precursors. However, while it can provide an initial indication of performance, the closer proximity of the other trendlines with their corresponding specific precursors indicates that it is difficult to create a unique equation englobing all types of alkali-activated binders.

The amount of data available in the literature can be used in an attempt to derive new analytical correlations between the compressive strength and other mechanical properties. However, due to the variability and complexity of the reaction process, a unique set of general equations covering all the possible mix design formulations, based exclusively on correlation of mechanical properties, cannot be derived. It is fundamental not only to consider the chemical composition of the binder, in particular its CaO and amorphous phases contents, but also the composition and dosage of the alkaline solutions, which play a fundamental role in the development of the mechanical performance of the material. This can be easily seen in Fig. 3, where new correlations to estimate the modulus of elasticity and the tensile strength have been derived using the equation type generalised in Eq. (1) and (2), respectively, for high- and low-calcium systems.

$$E_c = a \cdot 21.5 \cdot \left(\frac{f_{cm}}{10}\right)^{1/3}$$
(1)

$$f_{ctm} = b \cdot (f_{cm})^{2/3}$$
 (2)

As shown in Fig. 3a-3b, for both high- and low-calcium systems, a < 1, to demonstrate how the modulus of elasticity is generally lower for AAC compared to PCC. Table 8 collects the derived parameters, a and b, and the related R<sup>2</sup> value for high- and low-calcium systems.

 Table 8. Proposed parameters for Eq. (1) and (2) for alkali-activated systems.

Parameter	GGBFS	FA-C	FA-	FA-	Blende
			F_HT	F_RT	d
а	15.864	17.421	12.531	14.548	14.480
R <sup>2</sup>	0.356	0.379	0.434	0.156	0.135
b	0.306	0.277	0.212	0.297	0.255
R <sup>2</sup>	0.408	0.296	0.853	0.538	0.373

Despite the high number of data points, the R<sup>2</sup> is lower than 0.43, showing how the simple classification of the material according to the CaO content is not sufficient to describe the behaviour of AAC. The same can be observed for the tensile strength, as shown in Fig. 3c-3d. The high scatter between data points collected for the same binder type indicates how also the chemistry and the amount of the activators significantly affect the mechanical properties of the material. Thus, additional investigations evaluating, not only the binder chemistry, but also the characteristics of the alkaline solution used, need to be carried out to derive analytical equations able to correlate the chemistry of the mix formulation with the mechanical properties of the hardened concrete.



Figure 3. New correlation to predict the modulus of elasticity (a-b) and the tensile strength (c-d) from the compressive strength of high- and low-calcium systems (see Appendix).

It is important to state that, the absolute experimentally obtained values of all of the mechanical properties of AACs analyzed in this present work is, in general, sufficiently high according to minimal requirements of PCC-based design codes. In addition, despite the poor overall agreement in between compressive strength and modulus of elasticity and tensile strength for all of the collected data, it was possible to visualize similar trends in the correlation of properties when high- and low-Ca binders were evaluated individually. In addition, despite the poor overall agreement in between compressive strength and modulus of elasticity and tensile strength for all of the collected data, it was possible to visualize similar trends in the correlation of properties when high- and low-Ca binders were evaluated individually. Therefore, the adoption of performance-based standards, along with the determination of classes of binders, based on the mineralogical and chemical characteristics of precursors and activators, can represent a strong opportunity and an important step towards growth of the commercial potential of AACs.

#### 6 Conclusions

The need to achieve carbon neutrality by 2050 has increased interest in alkali-activated binders as a more environmentally friendly alternative to traditional cement-based binders in the construction sector. Recent investigations provided not only a better understanding of the technology from a chemical, physical and mechanical point of view but also raised awareness of the additional steps necessary for the adoption of alkali-activated concretes on the European and international markets. Despite being the subject of research for decades, with positive characteristics compared to traditional construction materials, the significant number of complexities involved in the whole production chain creates a barrier to the AAC's utilisation in large-scale projects. To overcome the existing barriers to the standardisation of AACs and to broaden their application as reliable structural engineering materials, a few challenges need to be faced:

- The classification in high- and low-calcium alkaliactivated systems, based on the CaO content of the binder, with 10 wt% being the threshold value, can be used to easily distinguish the different reaction mechanisms and related products, i.e. C-A-S-H and N-A-S-H gels, respectively, but is not sufficient to predict the mechanical performance of the systems.
- Due to the varying amounts of CaO reactive fraction and amorphous phases in the precursors, differing mechanical performance can be developed by concretes obtained by alkali-activation of binders with comparable CaO content and same activators quantities and proportions. A possible way to provide a more accurate classification of the binders suitable for alkali-activated concrete and an easier prediction of its short and long-term behaviour is to couple the CaO content with the amount of its reactive fraction and the content of amorphous phases in the binder.
- Although a more accurate classification of the binder is necessary to better understand and predict its behaviour during the reaction process, it is essential to consider also the characteristics of the alkaline solutions when defining the concrete mix design. The alkali content and silica modulus of the solutions can be adjusted and tailored according to the binder type to achieve the required material mechanical and durability performance, enabling the fit-to-purpose production of alkali-activated concrete.
- New analytical correlations based on the main characteristics of both binder and alkaline solutions need to be developed to predict the mechanical performance of the material, in particular the modulus of elasticity and tensile strength, from its compressive strength to promote the formulation of design regulations suitable for alkali-activated concrete.
- Performance-based over prescriptive standards and building regulations need to be preferred to facilitate the standardisation, commercialisation and adoption of alternative construction materials such as alkaliactivated concrete. Although in the last decade several alkali-activated systems-based products have become available on the market, dedicated standards at an international level are still missing, but highly necessary.

Overcoming the challenges briefly summarised in this study is certainly not an easy task to accomplish. Future investigations need to focus on a better understanding of how the chemistry of the mix design components affects the reaction mechanisms of conventional and non-conventional binders and the mechanical and durability performance of alkaliactivated concretes. Only deriving new analytical correlations between mechanical properties according to the chemistry of the system can promote the drafting of design guidelines and regulations and favour the adoption of AACs. Construction industries also play a fundamental role in not only further promoting the development of fit-to-purpose marketable mix design formulations but also building pilots and real-scale projects to validate the material performance and raise awareness of its potential. This would be additionally facilitated by the adoption of performance-based standards, which require newly developed construction materials to match or exceed the mechanical and long-term behaviour of traditional concrete, without defining specific mix design components or proportions. Only continuous advances in all the above-mentioned sectors can lead to the standardisation and commercialisation of alkali-activated concrete on a global market level.

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#### Authorship statement (CRediT)

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#### References

- D. Hodgson, P. Hugues, T. Vass, Cement, IEA Report 2022 (2022), IEA, Paris. https://www.iea.org/reports/cement.
- [2] Cembureau, Cementing the European Green Deal, Reaching Climate Neutrality along the Cement and Concrete Value Chain by 2050 (2020). <u>https://cembureau.eu/media/kuxd32gi/cembureau-2050roadmap\_final-version\_web.pdf</u>
- [3] A. Favier, C. De Wolf, K. Scrivener, G. Habert, A sustainable future for the European Cement and Concrete Industry: Technology assessment for full decarbonisation of the industry by 2050, ETH Zurich, 2018.
- [4] J.S.J. Van Deventer, D.G. Brice, S.A. Bernal, J.L. Provis, Development, standardization, and applications of alkali-activated concretes, ASTM Spec. Tech. Publ. STP 1566 (2013) 196-212. https://doi.org/10.1520/STP156620120083
- [5] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. Van Deventer, Geopolymer technology: The current state of the art, J. Mater. Sci. 42 (2007) 2917-2933. https://doi.org/10.1007/s10853-006-0637-z
- [6] A. Adesina, Performance and sustainability overview of alkaliactivated self-compacting concrete, Waste Dispos. Sustain. Energy. 2 (2020) 165-175. https://doi.org/10.1007/s42768-020-00045-w
- [7] J.L. Provis, F. Winnefeld, Outcomes of the round robin tests of RILEM TC 247-DTA on the durability of alkali-activated concrete, in: Proceedings of the International Conference on Concrete Repair, Rehabilitation and Retrofitting (ICCRRR 2018), Cape Town, South Africa, MATEC Web of Conferences 199 (2018) 02024. https://doi.org/10.1051/matecconf/201819902024
- [8] M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, Cem. Concr. Res. 41 (2011) 1232-1243. <u>https://doi.org/10.1016/j.cemconres.2010.11.012</u>
- [9] Y. Li, X. Min, Y. Ke, D. Liu, C. Tang, Preparation of red mud-based geopolymer materials from MSWI fly ash and red mud by mechanical activation, Waste Manag. 83 (2019) 202-208. <u>https://doi.org/10.1016/j.wasman.2018.11.019</u>

- [10] J. Rivera, F. Castro, A. Fernández-Jiménez, N. Cristelo, Alkali-Activated Cements from Urban, Mining and Agro-Industrial Waste: State-ofthe-art and Opportunities, Waste and Biomass Valorization. 12 (2021) 2665-2683. <u>https://doi.org/10.1007/s12649-020-01071-9</u>
- [11] S.A. Bernal, E.D. Rodríguez, A.P. Kirchheim, J.L. Provis, Management and valorisation of wastes through use in producing alkali - activated cement materials, J. Chem. Technol. Biotechnol. 91 (2016) 2365-2388. <u>https://doi.org/10.1002/jctb.4927</u>
- [12] C. Lu, Z. Zhang, C. Shi, N. Li, D. Jiao, Q. Yuan, Rheology of alkaliactivated materials: A review, Cem. Concr. Compos. 121 (2021) 104061. <u>https://doi.org/10.1016/i.cemconcomp.2021.104061</u>
- [13] A. Herrmann, A. Koenig, F. Dehn, Structural concrete based on alkaliactivated binders: Terminology, reaction mechanisms, mix designs and performance, Struct. Concr. 19 (2018) 918-929. https://doi.org/10.1002/suco.201700016
- [14] P. Duxson, J.L. Provis, Designing precursors for geopolymer cements, J. Am. Ceram. Soc. 91 (2008) 3864-3869. <u>https://doi.org/10.1111/j.1551-2916.2008.02787.x</u>
- [15] J.C.B. Moraes, M.M. Tashima, J.L. Akasaki, J.L.P. Melges, J. Monzó, M. V Borrachero, L. Soriano, J. Payá, Effect of sugar cane straw ash (SCSA) as solid precursor and the alkaline activator composition on alkaliactivated binders based on blast furnace slag (BFS), Constr. Build. Mater. 144 (2017) 214-224. https://doi.org/10.1016/j.conbuildmat.2017.03.166
- [16] I.I. Bashar, U.J. Alengaram, M.Z. Jumaat, A. Islam, H. Santhi, A. Sharmin, Engineering properties and fracture behaviour of high volume palm oil fuel ash based fibre reinforced geopolymer concrete, Constr. Build. Mater. 111 (2016) 286-297. https://doi.org/10.1016/j.conbuildmat.2016.02.022
- [17] S.A. Bernal, E.D. Rodríguez, R. Mejia de Gutiérrez, J.L. Provis, S. Delvasto, Activation of metakaolin/slag blends using alkaline solutions based on chemically modified silica fume and rice husk ash, Waste Biomass Valoriz. 3 (2012) 99-108. https://doi.org/10.1007/s12649-011-9093-3
- [18] Y. Liu, C. Shi, Z. Zhang, N. Li, An overview on the reuse of waste glasses in alkali-activated materials, Resour. Conserv. Recycl. 144 (2019) 297-309. <u>https://doi.org/10.1016/j.resconrec.2019.02.007</u>
- [19] A. Maldonado-Alameda, J. Giro-Paloma, A. Svobodova-Sedlackova, J. Formosa, J.M. Chimenos, Municipal solid waste incineration bottom ash as alkali-activated cement precursor depending on particle size, J. Clean. Prod. 242 (2020) 118443. <u>https://doi.org/10.1016/j.jclepro.2019.118443</u>
- [20] N.H. Thang, N.N. Hoa, D.T. Vu, P.T. Kien, M.A.B. Promentilla, Properties of geopolymer from coal bottom ash and water glass solution, Proceedings of the 23rd Regional Symposium on Chemical Engineering, Vung Tao City, Vietnam (2016), paper S03-26.
- [21] M.C. Bignozzi, L. Barbieri, I. Lancellotti, New geopolymers based on electric arc furnace slag. Adv. Sci. Technol. 69(2010) 117-122. <u>https://doi.org/10.4028/www.scientific.net/AST.69.117</u>
- [22] I.G. Lodeiro, N. Cristelo, A. Palomo, A. Fernández-Jiménez, Use of industrial by-products as alkaline cement activators, Constr. Build. Mater. 253 (2020) 119000.
  - https://doi.org/10.1016/j.conbuildmat.2020.119000
- [23] K. Gong, C.E. White, Impact of chemical variability of ground granulated blast-furnace slag on the phase formation in alkaliactivated slag pastes, Cem. Concr. Res. 89 (2016) 310-319. <u>https://doi.org/10.1016/j.cemconres.2016.09.003</u>
- [24] M.E. Natali, C.E. White, M.C. Bignozzi, Elucidating the atomic structures of different sources of fly ash using X-ray and neutron PDF analysis, Fuel. 177 (2016) 148-156. https://doi.org/10.1016/j.fuel.2016.03.017
- [25] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, Alkali-activated binders: A review: Part 1. Historical background, terminology, reaction mechanisms and hydration products, Constr. Build. Mater. 22 (2008) 1305-1314. <u>https://doi.org/10.1016/j.conbuildmat.2007.10.015</u>
- [26] R.J. Myers, S.A. Bernal, R. San Nicolas, J.L. Provis, Generalized structural description of calcium-sodium aluminosilicate hydrate gels: The cross-linked substituted tobermorite model, Langmuir. 29 (2013) https://doi.org/10.1021/la4000473
- [27] J.L. Provis, S.A. Bernal, Geopolymers and related alkali-activated materials, Annu. Rev. Mater. Res. 44 (2014) 299-327. https://doi.org/10.1146/annurev-matsci-070813-113515
- [28] V. Živica, Effects of type and dosage of alkaline activator and temperature on the properties of alkali-activated slag mixtures, Constr. Build. Mater. 21 (2007) 1463-1469. https://doi.org/10.1016/j.conbuildmat.2006.07.002

- [29] T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Effect of elevated temperature curing on properties of alkali-activated slag concrete, Cem. Concr. Res. 29 (1999) 1619-1625. https://doi.org/10.1016/S0008-8846(99)00143-X
- [30] X. Jiang, R. Xiao, Y. Bai, B. Huang, Y. Ma, Influence of waste glass powder as a supplementary cementitious material (SCM) on physical and mechanical properties of cement paste under high temperatures, J. Clean. Prod. 340 (2022) 130778. https://doi.org/10.1016/j.jclepro.2022.130778
- [31] X. Jiang, Y. Zhang, R. Xiao, P. Polaczyk, M. Zhang, W. Hu, Y. Bai, B. Huang, A comparative study on geopolymers synthesized by different classes of fly ash after exposure to elevated temperatures, J. Clean. Prod. 270 (2020) 122500. https://doi.org/10.1016/j.jclepro.2020.122500
- [32] M.T. Junaid, O. Kayali, A. Khennane, J. Black, A mix design procedure for low calcium alkali activated fly ash-based concretes, Constr. Build. Mater. 79 (2015) 301-310.
- https://doi.org/10.1016/j.conbuildmat.2015.01.048
- [33] N. Li, C. Shi, Z. Zhang, D. Zhu, H.-J. Hwang, Y. Zhu, T. Sun, A mixture proportioning method for the development of performance-based alkali-activated slag-based concrete, Cem. Concr. Compos. 93 (2018) 163-174. <u>https://doi.org/10.1016/j.cemconcomp.2018.07.009</u>
- [34] S.A. Bernal, J.L. Provis, B. Walkley, R. San Nicolas, J.D. Gehman, D.G. Brice, A.R. Kilcullen, P. Duxson, J.S.J. Van Deventer, Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation, Cem. Concr. Res. 53 (2013) 127-144. https://doi.org/10.1016/j.cemconres.2013.06.007
- [35] T. Xie, P. Visintin, X. Zhao, R. Gravina, Mix design and mechanical properties of geopolymer and alkali activated concrete: Review of the state-of-the-art and the development of a new unified approach, Constr. Build. Mater. 256 (2020) 119380. https://doi.org/10.1016/j.conbuildmat.2020.119380
- [36] Z. Zhang, J.L. Provis, J. Zou, A. Reid, H. Wang, Toward an indexing approach to evaluate fly ashes for geopolymer manufacture, Cem. Concr. Res. 85 (2016) 163-173. https://doi.org/10.1016/j.cemconres.2016.04.007
- [37] B. Sun, Y. Sun, G. Ye, G. De Schutter, A mix design methodology of slag and fly ash-based alkali-activated paste, Cem. Concr. Compos. 126 (2022) 104368.
- https://doi.org/10.1016/j.cemconcomp.2021.104368 [38] T.C. Powers, T.L. Brownyard, Studies of the physical properties of bardward Partiand compart pacts. ACL J Proc. 42 (1046) 101 122
- hardened Portland cement paste, ACI J. Proc., 43 (1946) 101-132. https://doi.org/10.14359/15302
- [39] K. Van Breugel, Numerical simulation of hydration and microstructural development in hardening cement-based materials (I) theory, Cem. Concr. Res. 25 (1995) 319-331. https://doi.org/10.1016/0008-8846(95)00017-8
- [40] G.S. Ryu, Y.B. Lee, K.T. Koh, Y.S. Chung, The mechanical properties of fly ash-based geopolymer concrete with alkaline activators, Constr. Build. Mater. 47 (2013) 409-418. https://doi.org/10.1016/j.conbuildmat.2013.05.069

[41] S. Aydın, B. Baradan, Effect of activator type and content on

- [41] S. Ayun, B. Baradan, Energy of activator type and content on properties of alkali-activated slag mortars, Compos. Part B Eng. 57 (2014) 166-172. https://doi.org/10.1016/j.compositesb.2013.10.001
- [42] J.L. Provis, J.S.J. Van Deventer, Alkali activated materials: state-of-theart report of RILEM TC 224-AAM, Springer/RILEM, Dordrecht (2014). <u>https://doi.org/10.1007/978-94-007-7672-2</u>
- [43] A. Buchwald, M. Vanooteghem, E. Gruyaert, H. Hilbig, N. De Belie, Purdocement: application of alkali-activated slag cement in Belgium in the 1950s, Mater. Struct. Constr. 48 (2015) 501-511. <u>https://doi.org/10.1617/s11527-013-0200-8</u>
- [44] The Zeobond Group, https://www.Zeobond.com. (n.d.).
- [45] Wagners, https://www.Wagner.com.au. (n.d.).
- [46] B. Tempest, C. Snell, T. Gentry, M. Trejo, K. Isherwood, Manufacture of full-scale geopolymer cement concrete components: A case study to highlight opportunities and challenges., PCI J. 60 (2015) 39-50. <u>https://doi.org/10.15554/pcij.11012015.39.50</u>
- [47] K. Yang, C. Yang, J. Zhang, Q. Pan, L. Yu, Y. Bai, First structural use of site-cast, alkali-activated slag concrete in China, Proc. ICE - Struct. Build. 171 (2018) 800-809. https://doi.org/10.1680/jstbu.16.00193
- [48] DB Group, https://Dbgholdings.com/Cemfree/ (n.d.).
- [49] RAMAC, https://www.Ramacreadymix.nl (n.d.).
- [50] EXEGY, (n.d.). <u>https://doi.org/https://www.soletanche-bachy.com/en/news/exegy-by-soletanche-bachy-first-ultra-low-carbon-concrete-foundation-barrette.</u>
- [51] Cemex, Vertua, <u>https://www.Cemex.co.uk/Vertua-Low-Carbon-Concrete</u>. (n.d.).

- [52] Blockwalls, https://www.Blockwalls.co.uk. (n.d.).
- [53] J.L. Provis, Alkali-activated cements and concretes Durability testing to underpin standardisation, Proceedings of the Sixth International Conference on Durability of Concrete Structures, Leeds, UK (2019), 16-26.
- [54] A. Shayan, Specification of geopolymer concrete: general guide, Austroads Project TS1835, Sydney (2016).
- [55] Austroads, Austroads Technical Specification ATS 5330 Supply of Geopolymer Concrete, 2020.
- [56] A. Dehghani, F. Aslani, N.G. Panah, Effects of initial SiO2/Al2O3 molar ratio and slag on fly ash-based ambient cured geopolymer properties, Constr. Build. Mater. 293 (2021) 123527. <u>https://doi.org/10.1016/j.conbuildmat.2021.123527</u>
- [57] Y. Ma, Microstructure and engineering properties of alkali activated fly ash-as an environment friendly alternative to Portland cement. Ph.D. thesis, TU Delft, Netherlands (2013).
- [58] S. Ramanathan, M. Croly, P. Suraneni, Comparison of the effects that supplementary cementitious materials replacement levels have on cementitious paste properties, Cem. Concr. Compos. 112 (2020) 103678. <u>https://doi.org/10.1016/i.cemconcomp.2020.103678</u>
- [59] Z. Li, B. Delsaute, T. Lu, A. Kostiuchenko, S. Staquet, G. Ye, A comparative study on the mechanical properties, autogenous shrinkage and cracking proneness of alkali-activated concrete and ordinary Portland cement concrete, Constr. Build. Mater. 292 (2021) 123418. https://doi.org/10.1016/j.conbuildmat.2021.123418
- [60] H. Ye, A. Radlińska, Quantitative analysis of phase assemblage and chemical shrinkage of alkali-activated slag, J. Adv. Concr. Technol. 14 (2016) 245-260. <u>https://doi.org/10.3151/jact.14.245</u>
- [61] H. Taghvayi, K. Behfarnia, M. Khalili, The effect of alkali concentration and sodium silicate modulus on the properties of alkali-activated slag concrete, J. Adv. Concr. Technol. 16 (2018) 293-305. <u>https://doi.org/10.3151/jact.16.293</u>
- [62] S.A. Bernal, The resistance of alkali-activated cement-based binders to carbonation. In: Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead, eds. F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (2015), pp. 319-332. https://doi.org/10.1533/9781782422884.3.319
- [63] S. Chithiraputhiran, N. Neithalath, Isothermal reaction kinetics and temperature dependence of alkali activation of slag, fly ash and their blends, Constr. Build. Mater. 45 (2013) 233-242. https://doi.org/10.1016/i.conbuildmat.2013.03.061
- [64] P. Chindaprasirt, T. Cao, Setting, segregation and bleeding of alkaliactivated cement, mortar and concrete binders, In: Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead, eds. F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (2015), 113-131. https://doi.org/10.1533/9781782422884.2.113
- [65] A. Kusbiantoro, M.F. Nuruddin, N. Shafiq, S.A. Qazi, The effect of microwave incinerated rice husk ash on the compressive and bond strength of fly ash based geopolymer concrete, Constr. Build. Mater. 36 (2012) 695-703.
  - https://doi.org/10.1016/j.conbuildmat.2012.06.064
- [66] R. Embong, A. Kusbiantoro, N. Shafiq, M.F. Nuruddin, Strength and microstructural properties of fly ash based geopolymer concrete containing high-calcium and water-absorptive aggregate, J. Clean. Prod. 112 (2016) 816-822.
- https://doi.org/10.1016/j.jclepro.2015.06.058
- [67] R. Si, S. Guo, Q. Dai, J. Wang, Atomic-structure, microstructure and mechanical properties of glass powder modified metakaolin-based geopolymer, Constr. Build. Mater. 254 (2020) 119303. https://doi.org/10.1016/j.conbuildmat.2020.119303
- [68] X. Gao, B. Yuan, Q.L. Yu, H.J.H. Brouwers, Characterization and application of municipal solid waste incineration (MSWI) bottom ash and waste granite powder in alkali activated slag, J. Clean. Prod. 164 (2017) 410-419. <u>https://doi.org/10.1016/j.jclepro.2017.06.218</u>
- [69] N. Hammad, A. El-Nemr, H.E.-D. Hasan, The performance of fiber GGBS based alkali-activated concrete, J. Build. Eng. 42 (2021) 102464. <u>https://doi.org/10.1016/i.jobe.2021.102464</u>
- [70] Y. Ding, J.-G. Dai, C.-J. Shi, Fracture properties of alkali-activated slag and ordinary Portland cement concrete and mortar, Constr. Build. Mater. 165 (2018) 310-320. <u>https://doi.org/10.1016/j.conbuildmat.2017.12.202</u>
- [71] M. Olivia, H. Nikraz, Properties of fly ash geopolymer concrete designed by Taguchi method, Mater. Des. 36 (2012) 191-198. https://doi.org/10.1016/j.matdes.2011.10.036

- [72] N. Nikoloutsopoulos, A. Sotiropoulou, G. Kakali, S. Tsivilis, Physical and Mechanical Properties of Fly Ash Based Geopolymer Concrete Compared to Conventional Concrete, Buildings. 11 (2021) 178. <u>https://doi.org/10.3390/buildings11050178</u>
- [73] M.T. Ghafoor, Q.S. Khan, A.U. Qazi, M.N. Sheikh, M.N.S. Hadi, Influence of alkaline activators on the mechanical properties of fly ash based geopolymer concrete cured at ambient temperature, Constr. Build. Mater. 273 (2021) 121752. https://doi.org/10.1016/j.conbuildmat.2020.121752
- [74] R.J. Thomas, S. Peethamparan, Alkali-activated concrete: Engineering properties and stress-strain behavior, Constr. Build. Mater. 93 (2015) 49-56. <u>https://doi.org/10.1016/i.conbuildmat.2015.04.039</u>
- [75] T.A. Aiken, J. Kwasny, W. Sha, K.T. Tong, Mechanical and durability properties of alkali-activated fly ash concrete with increasing slag content, Constr. Build. Mater. 301 (2021) 124330. https://doi.org/10.1016/j.conbuildmat.2021.124330
- [76] Z. Zhang, H. Wang, Alkali-activated cements for protective coating of OPC concrete. In: Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead, eds. F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (2015), pp. 605-626. <u>https://doi.org/10.1533/9781782422884.4.605</u>
- [77] A.M. Fernandez-Jimenez, A. Palomo, C. Lopez-Hombrados, Engineering properties of alkali-activated fly ash concrete, ACI Mater. J. 103 (2006) 106-112. https://doi.org/10.14359/15261
- [78] H. El-Hassan, A. Hussein, J. Medljy, T. El-Maaddawy, Performance of Steel Fiber-Reinforced Alkali-Activated Slag-Fly Ash Blended Concrete Incorporating Recycled Concrete Aggregates and Dune Sand, Buildings. 11 (2021) 327. <u>https://doi.org/10.3390/buildings11080327</u>
- [79] A.H. Mahmood, S.J. Foster, A. Castel, Effects of mixing duration on engineering properties of geopolymer concrete, Constr. Build. Mater. 303 (2021) 124449.
  - https://doi.org/10.1016/j.conbuildmat.2021.124449
- [80] G.F. Huseien, A.R.M. Sam, R. Alyousef, Texture, morphology and strength performance of self-compacting alkali-activated concrete: Role of fly ash as GBFS replacement, Constr. Build. Mater. 270 (2021) 121368. <u>https://doi.org/10.1016/i.conbuildmat.2020.121368</u>
- [81] Ü. Yurt, An experimental study on fracture energy of alkali activated slag composites incorporated different fibers, J. Build. Eng. 32 (2020) 101519. <u>https://doi.org/10.1016/i.jobe.2020.101519</u>
- [82] K.-H. Yang, J.-K. Song, A.F. Ashour, E.-T. Lee, Properties of cementless mortars activated by sodium silicate, Constr. Build. Mater. 22 (2008) 1981-1989. https://doi.org/10.1016/j.conbuildmat.2007.07.003
- [83] A.A. Aliabdo, M. Abd Elmoaty, M.A. Emam, Factors affecting the mechanical properties of alkali activated ground granulated blast furnace slag concrete, Constr. Build. Mater. 197 (2019) 339-355. https://doi.org/10.1016/j.conbuildmat.2018.11.086
- [84] H. El-Hassan, E. Shehab, A. Al-Sallamin, Influence of different curing regimes on the performance and microstructure of alkali-activated slag concrete, J. Mater. Civ. Eng. 30 (2018) 4018230. <u>https://doi.org/10.1061/(ASCE)MIT.1943-5533.0002436</u>
- [85] A. Wardhono, D.W. Law, T.C.K. Molyneaux, Long term performance of alkali activated slag concrete, J. Adv. Concr. Technol. 13 (2015) 187-192. <u>https://doi.org/10.3151/jact.13.187</u>
- [86] A. Wongkvanklom, P. Posi, A. Kampala, T. Kaewngao, P. Chindaprasirt, Beneficial utilization of recycled asphaltic concrete aggregate in high calcium fly ash geopolymer concrete, Case Stud. Constr. Mater. 15 (2021) e00615. <u>https://doi.org/10.1016/j.cscm.2021.e00615</u>
- [87] K. Ruengsillapanun, T. Udtaranakron, T. Pulngern, W. Tangchirapat, C. Jaturapitakkul, Mechanical properties, shrinkage, and heat evolution of alkali activated fly ash concrete, Constr. Build. Mater. 299 (2021) 123954. <u>https://doi.org/10.1016/j.conbuildmat.2021.123954</u>
- [88] Y.Y. Lim, T.M. Pham, J. Kumar, Sustainable alkali activated concrete with fly ash and waste marble aggregates: Strength and durability studies, Constr. Build. Mater. 283 (2021) 122795. <u>https://doi.org/10.1016/j.conbuildmat.2021.122795</u>
- [89] T. Phoo-Ngernkham, C. Phiangphimai, N. Damrongwiriyanupap, S. Hanjitsuwan, J. Thumrongvut, P. Chindaprasirt, A mix design procedure for alkali-activated high-calcium fly ash concrete cured at ambient temperature, Adv. Mater. Sci. Eng. 2018 (2018) 2460403. https://doi.org/10.1155/2018/2460403
- [90] P. Topark-Ngarm, P. Chindaprasirt, V. Sata, Setting time, strength, and bond of high-calcium fly ash geopolymer concrete, J. Mater. Civ. Eng. 27 (2015) 4014198.

https://doi.org/10.1061/(ASCE)MT.1943-5533.0001157

[91] E.I. Diaz-Loya, E.N. Allouche, S. Vaidya, Mechanical properties of flyash-based geopolymer concrete, ACI Mater. J. 108 (2011) 300-306. https://doi.org/10.14359/51682495

- [92] J. Pacheco, J. De Brito, C. Chastre, L. Evangelista, Scatter of constitutive models of the mechanical properties of concrete: Comparison of major international codes, J. Adv. Concr. Technol. 17 (2019) 102-125. <u>https://doi.org/10.3151/jact.17.102</u>
- [93] M. Komljenović, Mechanical strength and Young's modulus of alkaliactivated cement-based binders. In: Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead, eds. F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (2015), pp. 171-215. https://doi.org/10.1533/9781782422884.2.171
- [94] P. Nath, P.K. Sarker, Flexural strength and elastic modulus of ambientcured blended low-calcium fly ash geopolymer concrete, Constr. Build. Mater. 130 (2017) 22-31. https://doi.org/10.1016/j.conbuildmat.2016.11.034
- [95] N.K. Lee, H.-K. Lee, Setting and mechanical properties of alkaliactivated fly ash/slag concrete manufactured at room temperature, Constr. Build. Mater. 47 (2013) 1201-1209. <u>https://doi.org/10.1016/j.conbuildmat.2013.05.107</u>
- [96] J. Skibsted, M.D. Andersen, The effect of alkali ions on the incorporation of aluminum in the calcium silicate hydrate (C-S-H) phase resulting from Portland cement hydration studied by 29Si MAS NMR, J. Am. Ceram. Soc. 96 (2013) 651-656. <u>https://doi.org/10.1111/jace.12024</u>
- [97] A. Fernández Jiménez, F. Puertas, I. Sobrados, J. Sanz, Structure of calcium silicate hydrates formed in alkaline - activated slag: influence of the type of alkaline activator, J. Am. Ceram. Soc. 86 (2003) 1389-1394. <u>https://doi.org/10.1111/j.1151-2916.2003.tb03481.x</u>
- [98] I. Garcia-Lodeiro, A. Palomo, A. Fernández-Jiménez, D.E. MacPhee, Compatibility studies between N-A-S-H and C-A-S-H gels. Study in the ternary diagram Na2O-CaO-Al2O3-SiO-2-H2O, Cem. Concr. Res. 41 (2011) 923-931. <u>https://doi.org/10.1016/j.cemconres.2011.05.006</u>
- [99] J. Cai, X. Li, J. Tan, B. Vandevyvere, Thermal and compressive behaviors of fly ash and metakaolin-based geopolymer, J. Build. Eng. 30 (2020) 101307. <u>https://doi.org/10.1016/i.jobe.2020.101307</u>
- [100] K.-H. Yang, A.-R. Cho, J.-K. Song, Effect of water-binder ratio on the mechanical properties of calcium hydroxide-based alkali-activated slag concrete, Constr. Build. Mater. 29 (2012) 504-511. <u>https://doi.org/10.1016/j.conbuildmat.2011.10.062</u>

- [101] Y. Cui, K. Gao, P. Zhang, Experimental and statistical study on mechanical characteristics of geopolymer concrete, Materials (Basel). 13 (2020) 1651. <u>https://doi.org/10.3390/ma13071651</u>
- [102] M. Chi, Effects of dosage of alkali-activated solution and curing conditions on the properties and durability of alkali-activated slag concrete, Constr. Build. Mater. 35 (2012) 240-245. <u>https://doi.org/10.1016/j.conbuildmat.2012.04.005</u>
- [103] B.S. Gebregziabiher, R.J. Thomas, S. Peethamparan, Temperature and activator effect on early-age reaction kinetics of alkali-activated slag binders, Constr. Build. Mater. 113 (2016) 783-793. <u>https://doi.org/10.1016/j.conbuildmat.2016.03.098</u>
- [104] P. Nuaklong, V. Sata, A. Wongsa, K. Srinavin, P. Chindaprasirt, Recycled aggregate high calcium fly ash geopolymer concrete with inclusion of OPC and nano-SiO2, Constr. Build. Mater. 174 (2018) 244-252. https://doi.org/10.1016/j.conbuildmat.2018.04.123
- [105] D.H. Gray, Y.-K. Lin, Engineering properties of compacted fly ash, J. Soil Mech. Found. Div. 98 (1972) 361-380. https://doi.org/10.1061/JSFEAQ.0001744
- [106]S. Fang, E.S.S. Lam, B. Li, B. Wu, Effect of alkali contents, moduli and curing time on engineering properties of alkali activated slag, Constr. Build. Mater. 249 (2020) 118799.

https://doi.org/10.1016/j.conbuildmat.2020.118799

- [107] C.S. Thunuguntla, T.D. Gunneswara Rao, Effect of mix design parameters on mechanical and durability properties of alkali activated slag concrete, Constr. Build. Mater. 193 (2018) 173-188. https://doi.org/10.1016/j.conbuildmat.2018.10.189
- [108] C.-C. Hung, J.-J. Chang, The influence of mixture variables for the alkali-activated slag concrete on the properties of concrete, J. Mar. Sci. Technol. 21 (2013) 1.

#### Appendix

Table A.1. Summary of raw materials, mix design and mechanical properties (28-day compressive strength, tensile strength and modulus ofelasticity) collected from studies on alkali-activated fly ash-, slag- and fly ash/slag-based concretes and used as datapoints in Fig. 1, Fig. 2 and Fig.3.

Precursor	CaO (by mass % of - precursors)	Activator (kg/m³)		Characteristic	Tensile	Modulus of	
		NaOH	WG	compressive strength (MPa)	strength (MPa)	elasticity (GPa)	Ref.
FA-C	22.57	96.30	96.30	72.00	-	64.30	[86]
FA-C	22.57	117.70	117.70	55.30	-	57.20	[86]
FA-C	22.57	139.10	139.10	52.50	-	49.40	[86]
FA-C	22.57	160.50	160.50	41.00	-	39.50	[86]
FA-C	27.90	280.00	-	12.90	-	7.80	[87]
FA-C	27.90	215.00	65.00	18.70	-	12.80	[87]
FA-C	27.90	200.00	80.00	19.20	-	13.70	[87]
FA-C	27.90	187.00	93.00	33.40	-	18.90	[87]
FA-C	27.90	215.00	65.00	22.20	-	15.30	[87]
FA-C	27.90	215.00	65.00	25.10	-	16.10	[87]
FA-C	27.90	215.00	65.00	24.50	-	15.80	[87]
FA-C	27.90	200.00	80.00	27.10	-	16.70	[87]
FA-C	25.79	118.00	118.00	44.00	3.30	22.00	[89]
FA-C	25.79	113.00	113.00	41.00	3.18	26.00	[89]
FA-C	25.79	108.00	108.00	33.00	2.76	23.00	[89]
FA-C	25.79	118.00	118.00	40.00	3.66	23.00	[89]
FA-C	25.79	113.00	113.00	39.00	3.48	23.00	[89]
FA-C	25.79	108.00	108.00	34.00	3.30	23.00	[89]
FA-C	25.79	118.00	118.00	40.00	3.54	22.00	[89]
FA-C	25.79	113.00	113.00	38.00	3.06	24.00	[89]
FA-C	25.79	108.00	108.00	35.00	3.00	24.00	[89]

FA-C	25.79	118.00	118.00	33.00	2.88	24.50	[89]
FA-C	25.79	113.00	113.00	29.00	2.94	27.00	[89]
FA-C	25.79	108.00	108.00	28.00	2.46	25.00	[89]
FA-C	25.79	118.00	118.00	43.00	3.78	26.00	[89]
FA-C	25.79	113.00	113.00	40.00	3.72	26.00	[89]
FA-C	25.79	108.00	108.00	39.00	3.48	20.00	[89]
FA-C	25.79	118.00	118.00	44.00	3.78	26.00	[89]
FA-C	25.79	113.00	113.00	43.00	3.60	27.00	[89]
FA-C	25.79	108.00	108.00	41.00	3.48	26.00	[89]
FA-C	25.79	118.00	118.00	40.00	3 72	27.00	[89]
FA-C	25.79	113.00	113.00	41.00	3 48	28.00	[89]
FA-C	25.79	108.00	108.00	40.00	3 24	26.00	[89]
FA-C	25.79	118.00	118.00	26.00	3.60	19.00	[89]
FA-C	25.79	113.00	113.00	27.00	3.00	19.00	[89]
FA-C	25.79	108.00	108.00	24.00	3.06	29.00	[89]
FA-C	15 51	104.00	104.00	47.67	3 48	30.40	[90]
FA-C	15.51	104.00	104.00	54 67	3 74	31.00	[90]
FA-C	15.51	104.00	104.00	53 34	3 92	34.80	[90]
FA-C	15.51	104.00	104.00	62 40	4 47	37.80	[90]
FA-C	15.51	104.00	104.00	45.64	3 56	38.40	[90]
FA-C	15.51	104.00	104.00	51 42	3 99	38.00	[90]
FA-C	15.51	69.00	138.00	41.80	2 76	23.40	[90]
FA-C	15.51	69.00	138.00	48.09	3 26	24.20	[90]
FA-C	15.51	69.00	138.00	47.02	3.20	24.20	[90]
FA-C	15.51	69.00	138.00	56.18	3.63	31.00	[00]
FA-C	15.51	69.00	138.00	54.69	3.05	35.40	[00]
	15.51	69.00	128.00	57.50	2 50	21.80	[00]
FA-C	14.20	108.00	162.00	12 20	2.55	51.80	[30]
FA-C	14.20	108.00	162.00	43.20	2.01	-	[104]
FA-C	14.20	108.00	102.00	40.90 67 E0	2.45	-	[104]
FA-C	22.45	111.00	111.00	60.28	2.09	24.20	[91]
FA-C	12.07	98.00	98.00	62.80	2.03	27 11	[91]
FA-C	12.55	98.00	98.00	03.89	2.30	12 80	[91]
FA-C	10.72	96.00	96.00	60.57	2.10	42.09 21.4E	[91]
FA-C	25.55	98.00	98.00	09.38 17 10	2.50	10.07	[91]
FA-C	20.19	98.00	98.00	47.19	2.50	19.07	[91]
FA-C	22.20	98.00	98.00	01.70	2.00	26.91	[91]
FA-C	22.29 20 E2	98.00	98.00	44.34 CE 10	2.15	20.97	[91]
FA-C	20.33	90.00 122 EO	90.00 122 EO	03.10 E0.91	2 11	29.45	[91]
FA-C	20.47	123.30	123.50	70.10	2.00	22.57	[91]
FA-C	26.80	90.00 200.0E	90.00 200.05	10.19	2.90	1 97	[91]
	20.60	209.95	209.95	10.75	0.37	1.07	[91]
	2.24	81.00 72.00	100.00	45.55	2.70	21.10	[75]
	2.24	72.00	128.00	21.00	0.90	0.20 14.20	[75] [75]
	11.75	32.10	156.00	22.05 17 0C	2.34	14.50	[/2]
	11.75	40.20	232.00	42.00	1.90	17.10	[/2]
	11.75	04.50	330.00	42.05	2.25	17.50	[/2]
	2.44	217.00	37.00	55.45	-	17.10	[105]
	2.13	40.15	92.31	64.49	3.30	20.95	[/1]
	2.13	30.40	90.99	64.49	3.72	25.33	[/1]
	2.13	42.70	106.70	08.2U 49.2E	3.80	29.05	[/1]
	5.00	98.00	98.00		2.49	28.00	[91]
	5.48 F. C.4	98.00	98.00	55.55	3.35	29.47	[91]
	5.04 F 01	98.00	98.00	54.09	3.18	29.30	[91]
	5.01	98.00	98.00	54.79	2.77	28.52	[91]
	0.90 1.07	98.00	98.00	54.11	2.83	20.40	[91]
	1.97 F 42	123.50	123.50	20.20	3.07	20.04	[91]
	5.43	187.70	187.70	20.20	1.34	7.04	[91]
	4.69	232.10	232.10	20.82	1.43	7.00	[91]
	5.18	103.00	103.00	28.08	2.10	7.90	[91]
	5.57 A 6A	192.00	192.00	10.34 EA EC	1.04 2.70	7.40 20 77	[01]
	4.04	33.00 169.00	33.00 169.00	54.50 E7 34	5./9 2.90	20.74 10.29	[91]
	2.20	08.00	08.00	57.24 E1 30	2.80	13.79	[01]
	9.23	98.00	98.00	J1.3ŏ	2.54	23.01	[16]
	0.72		94.0U	10.90	1.08	10.80	[/3]
	0.72	52.50	105.10	17.20	1.50	7.30	[/3]
	0.72 6.72	45.00	112.60	10.00	1.50	7.00	[/3]
	0.72	/ 3.00	122.60	10.07	2.04	7.00 9.70	[/3] [72]
	0.72 6 70	01.3U	121.00	10.00	1.92	0.7U 7.40	[/3] נכק]
	0.72 6 70	52.5U	131.40	10.00	2.04	7.4U 10.50	[/3] נכק]
г <b>н-г_</b> КI	0.72	02.00	124.20	00.61	2.04	10.20	[/3]

	6.72	co oo	120.00	46.00	4 62	10.10	[70]
FA-F_KI	6.72	69.00	138.00	16.00	1.62	10.10	[/3]
FA-F_RT	6.72	59.10	147.80	16.00	1.56	8.80	[73]
FA-F RT	6.72	63.00	94.60	22.40	1.98	11.10	[73]
ΕΔ-E RT	6 72	52 50	105 10	21 90	2 52	10.00	[73]
	6.72	JZ.J0	105.10	21.50	2.52	10.00	[70]
FA-F_RI	6.72	45.00	112.60	21.10	1.56	17.40	[/3]
FA-F_RT	6.72	73.60	110.40	22.20	2.40	21.40	[73]
FA-F RT	6.72	61.30	122.60	20.90	2.34	15.10	[73]
	6.72	52.50	121.00	20.00	1.00	11 20	[70]
FA-F_KI	0.72	52.50	131.40	20.90	1.92	11.20	[/3]
FA-F_RT	6.72	82.80	124.20	21.00	2.10	19.10	[73]
FA-F RT	6.72	69.00	138.00	19.70	1.98	17.10	[73]
	6 72	50.10	1/7 80	10.90	1 0 2	11 20	[72]
IA-I_NI	0.72	59.10	147.00	19.80	1.92	11.20	[/3]
FA-F_RI	6.72	63.00	94.60	23.00	2.82	15.10	[/3]
FA-F_RT	6.72	52.50	105.10	22.50	2.04	7.80	[73]
FA-F RT	6 72	45.00	112 60	21.00	1 92	17 80	[73]
	6.72	72.60	110.40	25.00	2.52	22.20	[70]
FA-F_KI	0.72	/3.00	110.40	25.00	2.52	23.30	[/3]
FA-F_RT	6.72	61.30	122.60	23.00	2.52	15.10	[73]
FA-F RT	6.72	52.50	131.40	20.90	2.16	30.30	[73]
ΕΔ-E RT	6 72	82.80	124 20	20.50	2 82	27.20	[73]
	6.72	62.00	124.20	20.50	2.02	27.20	[70]
FA-F_RI	6.72	69.00	138.00	21.00	2.76	25.10	[/3]
FA-F_RT	6.72	59.10	147.80	20.70	2.10	15.50	[73]
FA-F RT	6.72	63.00	94.60	26.10	2.16	17.20	[73]
	6 72	52.50	105 10	26.00	2.00	28 50	[72]
	0.72	52.50	105.10	28.00	2.00	28.30	[/5]
FA-F_RT	6.72	45.00	112.60	25.50	2.10	28.50	[73]
FA-F RT	6.72	73.60	110.40	26.70	2.58	35.00	[73]
FΔ-F RT	6 72	61 30	122.60	28.90	3 00	30.10	[73]
	6.72	52.50	122.00	20.50	2.00	30.10	[70]
FA-F_KI	6.72	52.50	131.40	25.10	2.82	30.30	[/3]
FA-F_RT	6.72	82.80	124.20	29.50	2.82	27.70	[73]
FA-F RT	6.72	69.00	138.00	24.00	2.88	25.30	[73]
	6.72	F0 10	147.00	20.70	2.00	21.50	[70]
FA-F_KI	0.72	59.10	147.80	20.70	2.34	31.50	[/3]
FA-F_RT	6.72	63.00	94.60	24.80	2.40	10.60	[73]
FA-F RT	6.72	52.50	105.10	25.60	2.88	15.20	[73]
FΔ-F RT	6 72	45.00	112.60	25.00	2 40	14 50	[73]
	6.72	73.00	112.00	29.00	2.40	14.50	[70]
FA-F_KI	6.72	/3.60	110.40	29.50	3.00	35.20	[/3]
FA-F_RT	6.72	61.30	122.60	25.90	3.00	26.20	[73]
FA-F RT	6.72	52.50	131.40	23.80	2.94	28.10	[73]
EA-E RT	6 72	82.80	12/ 20	25.00	2 82	30.60	[72]
	6.72	62.00	124.20	23.00	2.02	30.00	[70]
FA-F_RI	6.72	69.00	138.00	23.50	2.94	14.50	[/3]
FA-F_RT	6.72	59.10	147.80	22.60	2.34	20.10	[73]
Blend	32.32	66.00	99.00	54.47	2.64	22.40	[78]
Pland	22.65	60.00	00.00	27.42	1.07	12.60	[70]
ыепа	22.05	60.00	99.00	37.42	1.97	12.00	[/8]
Blend	17.28	8.23	115.50	49.20	2.26	27.40	[79]
Blend	17.28	8.23	115.50	46.70	2.43	29.10	[79]
Blend	17 41	8 23	115 50	44 50	1 92	29.60	[79]
Dianal	17.11	0.20	115.50	12.20	2.02	20.00	[70]
Blend	17.41	8.23	115.50	42.30	2.22	30.30	[/9]
Blend	10.51	73.00	88.00	42.05	2.52	19.70	[75]
Blend	18.85	72.00	88.00	55.45	3.42	27.10	[75]
Pland	21 21	72.00	97.00	60 50	2 07	28.00	[75]
Dieliu	51.51	72.00	87.00	00.50	2.57	28.90	[/]]
Blend	51.80	138.30	103.80	65.54	5.76	27.00	[80]
Blend	37.81	138.30	103.80	63.66	5.31	26.20	[80]
Blend	33,14	138.30	103.80	62.58	4.95	25.00	[80]
Bland	28.48	138 20	103.80	60.25	1 86	24.00	[80]
	20.40	130.30	103.00	51.60	4.00	24.00	
Blend	23.82	138.30	103.80	51.68	4.68	23.00	[80]
Blend	19.15	138.30	103.80	44.79	4.23	22.80	[80]
GGBES	38.65	61.00	152.00	41.81	2.86	26.67	[69]
CORES	26.00	46.00	71.00	17 17		25.60	[0[]
GGDF3	30.00	40.00	/1.00	47.47	-	25.09	[05]
GGBFS	39.80	-	-	41.70	6.12	34.20	[74]
00050	22.22	_		50.70	c	26.22	[74]
GGBFS	39.80		-	52.70	6.48	26.20	
CODES	20 00	-		E4 70	E 67	27.00	[74]
GGRE2	59.80		-	54.70	5.07	27.00	
CORE	20.80	-		42.00	5 67	27 00	[74]
GOBES	39.80		-	43.00	3.07	27.90	
GGBES	39.80	-	-	53 70	7 47	22 40	[74]
30013	55.00			55.70	·/	22.70	[7 4]
GGBES	39.80	-	-	60.60	7.56	33.50	[/4]
COPES		12.60	22.20	25.00	1.00		[100]
GGDE3	43.33	12.00	22.70	33.23	4.30	-	[100]
GGBFS	45.55	10.40	34-00	39.78	4.68	-	[106]
GGBFS	45.55	8.20	45.30	40.19	4.62	-	[106]
GGBES	45 55	18 80	34.00	44 16	6 60	-	[106]
CODEC		10.00	5 1.00	F1 26	6.10		[100]
GOBES	43.33	12.20	00.00	51.30	0.12	-	[106]
GGBFS	45.55	12.30	67.50	54.31	5.40	-	[106]
GGBFS	45.55	24.90	45.10	61.25	6.12	-	[106]

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GGBFS	45.55	20.60	67.40	64.64	6.00	-	[106]
COPES		16.20	90 E0	67.60	E 0/		[106]
GGBF3	45.55	10.50	69.50	07.00	5.94	-	[100]
GGBFS	45.55	31.00	56.10	68.25	5.88	-	[106]
GGBFS	45.55	25.60	83.80	69.44	4.98	-	[106]
CORES	15 55	20.20	111 20	97.96	1 96		[106]
00013	45.55	20.20	111.20	82.80	4.80	-	[100]
GGBFS	45.55	37.10	67.10	68.09	5.28	-	[106]
GGBFS	45.55	30.50	100.10	80.31	4.62	-	[106]
CORES	15 55	24.10	122.80	85.00	1.69		[106]
00013	45.55	24.10	132.80	03.33	4.00	-	[100]
GGBFS	33.67	48.00	72.00	21.53	1.52	-	[107]
GGBFS	33.67	66.00	99.00	26.86	2.34	-	[107]
CORES	22.67	72.00	109.00	25.69	2.24		[107]
00013	33.07	72.00	108.00	23.08	2.24	-	[10/]
GGBFS	33.67	99.00	148.50	31.38	2.39	-	[107]
GGBFS	33.67	48.00	72.00	63.63	3.81	-	[107]
GGRES	33 67	66.00	99 00	66.45	1 15	_	[107]
	55.07	00.00	55.00	00:45		-	[107]
GGBFS	33.67	72.00	108.00	69.18	5.00	-	[107]
GGBFS	33.67	99.00	148.50	71.90	4.97	-	[107]
GGBES	33 30	8.00	49.00	41 45	3 78	20.00	[70]
00015	33.30	0.00	71.00	-1J	5.70	20.00	[70]
GGBFS	33.30	11.00	/1.00	50.94	4.59	22.00	[/0]
GGBFS	33.30	11.00	117.00	65.23	5.45	23.60	[70]
							[100]
GGBFS	45.00	-	-	24.60	1.05	13.01	[100]
							[100]
GGBFS	45.00	-	-	24.90	1.01	12.95	[100]
							[100]
GGBFS	45.00	-	-	27.40	1.34	18.77	[100]
							[100]
GGBFS	45.00	-	-	28.50	1.34	16.55	[]
							[100]
GGBFS	45.00	-	-	31.30	1.76	19.45	
							[100]
GGBFS	45.00	-	-	34.60	1.76	19.72	
CODEC	45.00	_	_	40.00	2.20	22.52	[100]
GGBFS	45.00			40.60	2.30	23.52	
CODEC	45.00	_	_	28.00	2 21	20.02	[100]
GGBFS	45.00			38.00	2.31	20.83	
CORES	45.00	-	-	40.20	2 20	21.62	[100]
00013	45.00			40.20	2.39	21.02	
GGBES	45.00	-	-	44 50	2 48	25 29	[100]
00015	13.00			11.50	2.10	23.23	[100]
GGBFS	45.00	-	-	53.10	2.84	29.91	[100]
000.0				50.20	2.0.	20101	[100]
GGBFS	45.00	-	-	58.20	2.95	31.47	[100]
COPES	20 54	222 220		12.05	2 21	10.20	[100]
GGBF3	59.54	227-339	-	45.05	5.21	19.20	[100]
GGBFS	39.54	227-339	-	44.00	3.22	19.60	[108]
GGBFS	39.54	227-339	-	44.60	3.27	19.70	[108]
COPES	20 54	227 220		44.72	2 21	10.70	[100]
GGBF3	59.54	227-339	-	44.72	5.51	19.70	[100]
GGBFS	39.54	227-339	-	45.45	3.53	19.70	[108]
GGBFS	39.54	227-339	-	46.56	3.71	19.85	[108]
CORES	20 51	227.220		17 56	2 7/	20.00	[100]
00013	33.34	227-339	-	47.50	5.74	20.00	[100]
GGBFS	39.54	227-339	-	48.07	3.60	20.30	[108]
GGBFS	39.54	227-339	-	48.96	3.83	20.80	[108]
CORES	20 54	222 220	_	10.22	2 76	20.65	[100]
00013	33.34	227-339	-	45.22	3.70	20.05	[100]
GGBFS	39.54	227-339	-	50.25	3.85	20.50	[108]
GGBFS	39.54	227-339	-	50.38	3.92	21.10	[108]
GGBES	39 54	227-339	-	50.64	3 90	21 35	[108]
CODES	33.54	227 333		50.04	3.50	21.35	[100]
GGBFS	39.54	227-339	-	52.22	4.19	21.30	[108]
GGBFS	39.54	227-339	-	54.65	4.39	21.50	[108]
GGBES	39.54	227-339	-	55.61	4.40	21.60	[108]
CODEC	30.54	227 333		55.01	1.10	21.00	[100]
GGBFS	39.54	227-339	-	54.51	4.21	21.70	[108]
GGBFS	43.34	58.18	101.82	44.42	3.49	22.92	[83]
GGBFS	43.34	42.35	137.65	43.72	3.41	20.92	[83]
CCDFC	12.24	F7 1 4	142.96	11.10	2.65	22.02	[00]
GGBF3	43.34	57.14	142.80	44.49	3.05	23.98	[83]
GGBFS	43.34	45.71	114.29	45.27	3.83	34.93	[83]
GGBFS	43.34	65.45	114.55	46.05	4.68	27.64	[83]
CORES	12 21	17.06	152 0/	16.92	1 02	22.19	[02]
	42.24	-7.00	102.04	-0.05	7.02	32.10	[03]
GGRES	43.34	45./1	114.29	48./4	3.//	20.98	[83]
GGBFS	43.34	48.00	132.00	49.54	3.62	26.21	[83]
GGBFS	43.34	72.73	127.27	50.34	3.75	28.96	[83]
GGRES	13 3/	37.65	122 35	51 1/	3 66	30.23	[92]
00013	-1.34	57.05	122.33	51.14	5.00	50.25	[02]
GGBFS	43.34	51.43	128.57	51.94	4.06	27.07	[83]
GGBFS	43.34	72.73	127.27	53.75	3.78	27.20	[83]
GGBES	43 34	58 18	101 82	54 57	4 02	35 11	[83]
	10.04	42.25	101.02	5	2.02	22.00	[00]
GGRES	43.34	42.35	137.65	55.39	3.82	33.69	[83]
GGBFS	43.34	57.14	142.86	56.21	3.76	24.99	[83]
GGBFS	43.34	45.71	114.29	57.03	4.17	37.83	[83]

GGBFS	43.34	65.45	114.55	58.77	3.66	23.19	[83]
GGBFS	43.34	47.06	152.94	59.60	3.80	22.91	[83]
GGBFS	43.34	45.71	114.29	60.43	3.83	29.32	[83]
GGBFS	43.34	65.45	114.55	61.27	3.77	21.17	[83]
GGBFS	43.34	47.06	152.94	62.10	4.18	37.46	[83]
GGBFS	43.34	37.65	122.35	62.93	4.10	35.33	[83]
GGBFS	43.34	51.43	128.57	63.77	4.50	31.44	[83]
GGBFS	43.34	72.73	127.27	63.76	3.57	22.99	[83]
GGBFS	43.34	58.18	101.82	64.58	3.65	26.19	[83]
GGBFS	43.34	42.35	137.65	65.40	4.51	38.57	[83]
GGBFS	43.34	57.14	142.86	66.22	3.32	19.66	[83]
GGBFS	40.67	13.00	46.50	46.78	3.06	-	[102]
GGBFS	40.67	16.30	58.10	49.75	3.51	-	[102]
GGBFS	40.67	19.50	69.70	53.80	3.47	-	[102]
GGBFS	40.67	13.00	46.50	56.30	3.51	-	[102]
GGBFS	40.67	16.30	58.10	55.85	3.60	-	[102]
GGBFS	40.67	19.50	69.70	57.75	3.96	-	[102]
GGBFS	40.67	13.00	46.50	60.60	4.23	-	[102]
GGBFS	40.67	16.30	58.10	60.05	3.87	-	[102]
GGBFS	40.67	19.50	69.70	58.90	3.60	-	[102]
GGBFS	40.67	13.00	46.50	58.20	3.78	-	[102]
GGBFS	40.67	16.30	58.10	63.00	3.96	-	[102]
GGBFS	40.67	19.50	69.70	64.75	4.05	-	[102]
GGBFS	40.67	13.00	46.50	65.86	3.83	-	[102]
GGBFS	40.67	16.30	58.10	65.95	4.32	-	[102]
GGBFS	40.67	16.30	58.10	65.70	4.41	-	[102]
GGBFS	40.67	19.50	69.70	67.40	4.50	-	[102]
GGBFS	42.00	70.00	177.00	43.40	-	21.20	[84]
GGBFS	42.00	64.00	161.00	56.44	-	25.65	[84]
GGBFS	42.00	58.00	145.00	62.61	-	28.95	[84]
GGBFS	42.00	70.00	177.00	75.57	-	32.30	[84]
GGBFS	42.00	64.00	161.00	76.23	-	32.70	[84]
GGBFS	42.00	57.00	145.00	77.06	-	32.90	[84]
GGBFS	42.00	70.00	177.00	79.91	-	33.60	[84]
GGBFS	42.00	64.00	161.00	82.13	-	35.00	[84]
GGBFS	42.00	57.00	145.00	82.65	-	35.30	[84]