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Maximising the benefits of calcium carbonate in sustainable cements: opportunities and challenges associated with alkaline waste carbonation

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Cement production significantly contributes to global climate change and implementation of carbon capture, utilisation and storage (CCUS) in construction materials is considered a crucial step toward achieving net-zero emissions. Substituting Portland cement (PC) clinker with limestone has been demonstrated to effectively reduce CO_2 emissions while enhancing the properties of cement and concrete. Beyond limestone extraction, quarrying, and crushing, various types of alkaline waste materials generated from industrial processes can serve as valuable resources for producing diverse forms of calcium carbonate, simultaneously capturing a substantial amount of CO_2. In this context, we contend that due to the distinct characteristics of various calcium carbonate forms, there exists the substantial potential to maximise their technical, economic, and environmental advantages in the production of sustainable cements. We reviewed existing studies of the effects of different calcium carbonate forms on cement properties and underscored the viability of utilising various alkaline wastes to produce different calcium carbonate products. As a promising approach for CO_2 reduction, waste management, and resource recovery, we addressed the opportunities and challenges associated with advancing CCUS through the utilisation of carbonated alkaline wastes in sustainable cements. To achieve real-world impacts, we emphasised the necessity for interdisciplinary research collaborations, active involvement from industry stakeholders, regulatory bodies, and governmental support to facilitate the large-scale adoption of these innovative practices.

INTRODUCTION

Cement production is a major contributor to global climate change, with 4.2 billion tonnes of cement produced in 2020, accounting for approximately 8% of anthropogenic CO_2 emissions[1,2]. An effective strategy for decarbonising the construction industry is to modify the cement composition with low-carbon materials such as natural minerals or industrial by-products to reduce the clinker proportion. The substitution of Portland cement (PC) clinker with limestone and supplementary cementitious materials (SCMs) has been widely adopted worldwide for decades, proving to be an effective means of offsetting CO_2 emissions while enhancing the properties of cement and concrete[3]. Extensive research has been conducted on the impact of limestone on the hydration and engineering properties of PC[4,5]. Limestone acts as a filler to provide additional surface for nucleation of the hydration phases such as calcium-silicate hydrates (C-S-H) and reduces the effective water-to-cement ratio, significantly shortening the induction period of PC hydration[6]. Simultaneously, it reacts with aluminate phases in PC to form hemicarbonate and monocarbonate, stabilising ettringite and resulting in an increase of the hydrates' volume and hence a lower porosity of hardened PC[7,8]. Limestone is inexpensive and readily available, constituting approximately 15% of all the sedimentary rocks in the earth's crust[9]. Its low-carbon footprint makes a higher replacement level in cement desirable from a sustainability perspective. Currently, up to 15 wt% and 30 wt% of limestone can be incorporated in blended cement as specified in ASTM C595[10] and EN 197-1[11], respectively. However, a high replacement level in PC is usually

associated with the dilution effect and poorer mechanical performance due to the limited aluminate phases in PC[12].

Calcium carbonate has three anhydrous crystalline polymorphs, namely vaterite, aragonite, and calcite with increasing thermodynamic stability. Amorphous calcium carbonate (ACC) has also been found in many living organisms[13]. While calcite is the main phase in limestone and is prevalent, other forms of calcium carbonate do not exist in nature abundantly. Nevertheless, all forms of calcium carbonate have been synthesised successfully via numerous methods with particular sizes, morphologies and compositions using a wide range of precursors[14]. The availability of calcium and carbonate ions and hence the proportions of calcium carbonate that actively participate in the reactions in cements depend on the solubility of calcium carbonate, which is not only affected by external conditions but also the properties of calcium carbonate. As depicted in Fig. 1, calcium carbonate has the capability of incorporating a substantial proportion of divalent ions[15,16] and its solubility spans over three orders of magnitude with varying dissolution kinetics, which would significantly affect their interactions with other phases in cements.

Furthermore, abundant alkaline wastes globally present a significant potential for carbon capture, utilisation and storage (CCUS)[17], especially if the carbonated products are utilised in construction materials[18], offering alternatives to mined limestone. Therefore, in the context of CCUS with alkaline wastes, we argue that there is substantial potential to maximise the technical, economic, and environmental benefits of calcium carbonates by leveraging their different forms. In the following sections, we will review the existing literature on the effects of different calcium carbonate forms on the cement properties (section "Cements with

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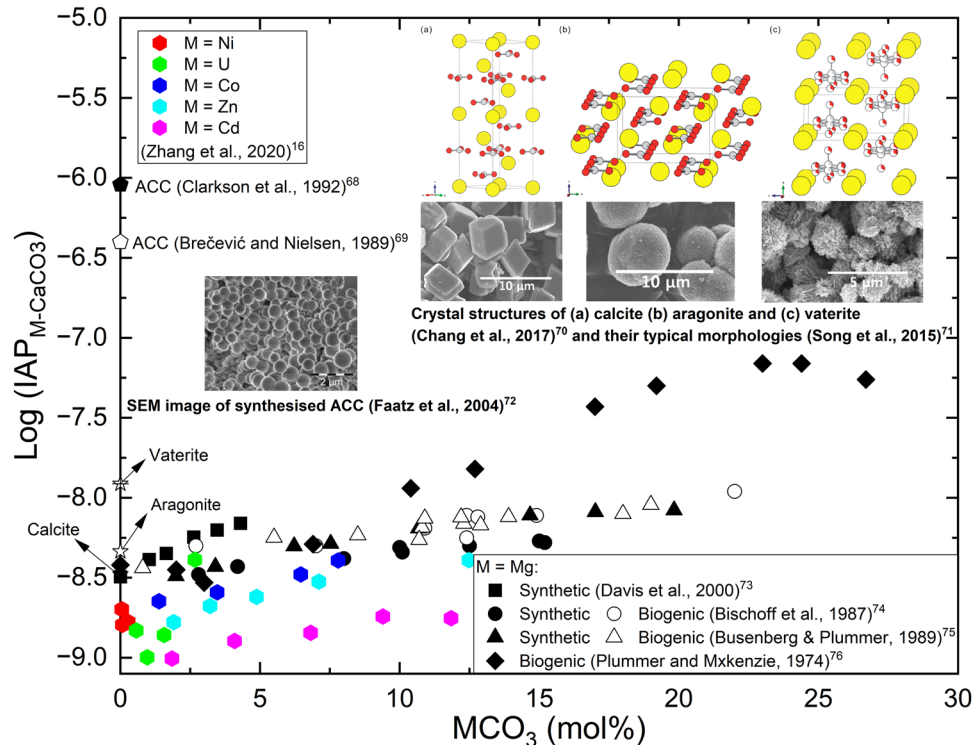
Fig. 1 Solubility (expressed as $IAP_{M-CaCO_3} = (a_{Ca^{2+}})(a_{CO_3^{2-}})$) of CaMCO$_3$ in the literature, where IAP is the ion activity product and **a** denotes activity of the ion in the solution[16,68–76]. The data for calcite, aragonite and vaterite are from Plummer & Busenberg (1982)[77].

different calcium carbonate forms") and present the current research fronts on utilising various alkaline wastes to produce diverse calcium carbonate products in Section "Controlling calcium carbonate polymorphism during alkaline waste carbonation". The opportunities and challenges of alkaline waste carbonation and their utilisation in cements will be discussed in sections "Process optimisation to achieve CCS, resource recovery and sustainable cements" and "Toward large-scale CCUS of alkaline wastes in sustainable cements." Finally, we call for interdisciplinary research to address the challenges and urge active engagement from the relevant industries, regulatory bodies and governments to facilitate CCUS of alkaline wastes in construction materials, thereby creating a global real-world impact.

CEMENTS WITH DIFFERENT CALCIUM CARBONATE FORMS

With the recognised reactive role of calcium carbonate in PC, there is a growing interest in harnessing various forms of calcium carbonate to enhance the performance of different cement types. In addition to investigating different calcium carbonate polymorphs and ACC[19,20], researchers have explored nanoparticles[21], unique morphologies[22] and dolomite[12] (note that dolomite is a different mineral but is shown here for comparison due to its relevant chemical composition and natural abundance). For instance, up to 15 wt% nano-sized calcite has been used and significantly improved the strength of PC[19] (Fig. 2a). Li et al.[22] compared the effects of aragonite and calcite on enhancing the early hydration and strength development of PC (Fig. 2a), confirming that although the two polymorphs have similar solubilities (see Fig.1), calcite is more effective than aragonite as it provides a favourable surface for nucleation and growth of calcium-silicate-hydrate (C-S-H, the main strength-giving phase in hydrated PC)[23]. Moreover, up to 15 wt% and 50 wt% limestone added in the PC-metakaolin blended cement and geopolymer, respectively, have resulted in enhanced strength[24,25] (Fig. 2b, c). In

the calcium sulfoaluminate (CSA) cement with 85 wt% ye'elimite and 15 wt% gypsum, vaterite has been found to exhibit greater reactivity than calcite when reacting with monosulfoaluminate, leading to strength improvements exceeding 25% at 28 days compared to CSA[26] (Fig. 2d).

The interactions between calcium carbonate and different cements are complex as shown in Fig. 2. With such a limited dataset, it is impossible to deduce meaningful trends due to the varying compositions of the cements and the diverse characteristics of the calcium carbonate employed in each study. Additionally, factors such as curing conditions[27], water to cement ratio[28] and other parameters influencing the cement hydration, rheological, chemical properties and durability are not covered here. Nevertheless, it is evident that: (i) different forms of calcium carbonates have distinct effects on cement hydration and engineering properties; (ii) up to 15 wt% of cement replacement generally has no adverse effect on cement strength; (iii) in cements with high aluminate contents, the differences between different calcium carbonate polymorphs are more pronounced and (iv) the reactivity of calcium carbonate can be effectively enhanced by increasing its surface area (although nanoparticles tend to agglomerate and disperse unevenly in the cement matrix, posing challenges to their real-world applications). In summary, the choice of the calcium carbonate form and its processing (i.e., size reduction, morphology control and polymorph tuning) can be tailored for specific applications to optimise the rheological, mechanical and chemical properties of cement-based materials. Their benefits may be further maximised in low-carbon cements such as geopolymers, supersulfated cements and limestone calcined clay cements. Furthermore, future research may explore the effects of magnesium carbonate or iron carbonate on the properties of different cement types as both elements are abundant in certain alkaline wastes[29,30].
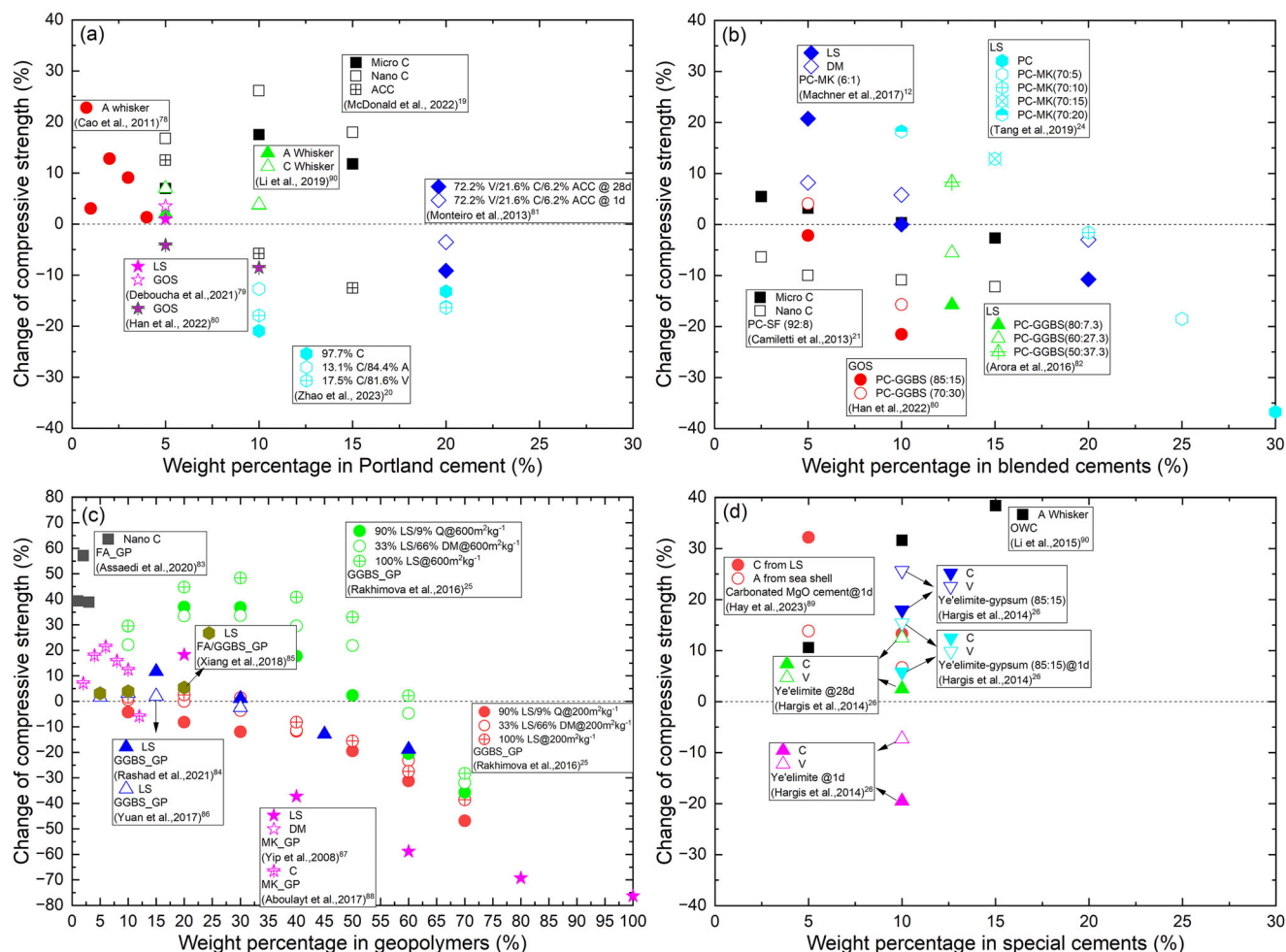
Fig. 2 Effect of calcium carbonate addition on the compressive strength of different types of cements[12,19–21,24–26,78–90]. These cements are shown in the subfigures: **a** Portland cement, **b** blended cements, **c** geopolymer and **d** special cements. Please note the different scales in subfigure **c**. Note: (i) all strength values are at 28 days unless specified in the figure; (ii) only the mineral compositions reported in the original studies were used; and (iii) the ratios shown in the legends indicate the compositions of the cements. SF silica fume, FA fly ash, GGBS ground granulated blast furnace slag, MK metakaolin, Q quartz, OWC oil well cement, GP geopolymer, LS limestone, DM dolomite, GOS ground oyster shell, C calcite, A aragonite, V vaterite, ACC amorphous calcium carbonate.

CONTROLLING CALCIUM CARBONATE POLYMORPHISM DURING ALKALINE WASTE CARBONATION

Numerous studies have reported the means of controlling the size, morphology and polymorphism of calcium carbonate during chemical synthesis. Interested readers can refer to Liendo et al.[31] and Niu et al.[14] for more in-depth insights. The promotion of green chemistry[32] and circular economy[33] are compelling researchers and industries to look towards different waste streams as potential precursors for generating valuable materials. Alkaline wastes such as slags, coal ashes and biomass ashes have been generated in vast quantities worldwide, both in the past and the present, with projections for future generation[17,34]. These waste materials present promising alternatives to natural silicate rocks for carbon capture and storage (CCS) while producing valuable carbonated products[35]. Using alkaline wastes for CCS offers several advantages including higher chemical reactivity, proximity to CO_2 point sources, and the potential to extract valuable metals while treating hazardous wastes[36]. They are either carbonated indirectly or directly; the former involves extraction of cations from the waste and their subsequent carbonation while in the latter, carbon dioxide reacts with the solid wastes either in gas-solid or aqueous carbonation mode[37]. High-quality calcium/magnesium carbonates can be obtained by optimising the operating parameters in indirect carbonation[38] while low-end applications of the carbonated products were common (e.g., as concrete aggregates and road substrates) after direct carbonation of alkaline wastes[39].

Waste materials have complex chemical compositions and calcium is typically bound to low solubility minerals and consequently aggressive leaching agents are commonly used to extract it. Although the leaching procedure is associated with high energy and reagent consumption, the CO_2 conversion rate is usually high and the characteristics of the final precipitated calcium carbonate could be readily adjusted by fine-tuning the wet carbonation conditions. On the other hand, direct carbonation occurs at the surface layer of the alkaline wastes, resulting in a lower CO_2 conversion rate but requiring minimal post-treatment (i.e., reagent recovery, wastewater and solid residue treatment and disposal). Due to the slow diffusion rate of CO_2 and low solubility of calcium-rich minerals (primarily calcium silicates), the final product often exhibits a core-shell structure with silica gel and carbonates covering the original material[40].

It is worth noting that for direct carbonation, little has been done to control the polymorphs of precipitated calcium carbonate, but the experimental results demonstrated their co-existence under specific carbonation conditions. For instance, Bodor et al.[41] and Liu et al.[42] showed that all crystalline calcium carbonate polymorphs and significant proportions of amorphous

phases were identified by quantitative XRD during direct carbonation of steel slags. It is well established that magnesium inhibits calcite crystallisation and promotes the formation of other phases including ACC[43,44]. Additionally, Lin et al.[45] demonstrated that inorganic surface functional groups have a similar ability to organic ones in selectively inducing metastable carbonate polymorph crystallisation, which was further supported in recent work by Shen et al.[46] that silica was able to stabilise ACC and inhibit its transformation to calcite. Consequently, a mixture of different polymorphs and ACC is commonly detected in carbonated wastes in the literature.

However, existing studies have primarily focused on maximising the CCS potentials of alkaline wastes and optimising the mechanical properties of cements with those carbonated products without taking into account the distinct properties of various calcium carbonate forms and their variable effects in different cement systems, as discussed in preceding sections. The main reasons could be: (i) an emphasis on CCS promotion rather than the production of value-added mineral additives for sustainable cements; (ii) the wide-ranging compositions of different alkaline wastes, coupled with the diverse experimental conditions, resulting in significant challenges in controlling the dissolution rate of calcium-rich mineral phases and the growth of carbonates; and (iii) a lack of in-situ experimental techniques to determine and quantify different $CaCO_3$ polymorphs. Therefore, we posited that diverse calcium carbonate forms can be produced by leveraging various alkaline wastes, offering opportunities for tailored material properties and environmental benefits. Recent studies have shown promising results in adjusting the carbonation conditions of cement powders and recycled concrete fines to produce aragonite whiskers as micro-fibres in cement, improving compressive and flexural strength significantly[46–48].

PROCESS OPTIMISATION TO ACHIEVE CCS, RESOURCE RECOVERY AND SUSTAINABLE CEMENTS

While the global potential of CCS using alkaline waste is immense, the process naturally proceeds slowly under ambient conditions[49] and hence accelerated carbonation has to be implemented with concentrated CO_2, aggressive chemical reagents and elevated temperature/pressure. Even under optimised conditions, the actual carbonation efficiency typically falls significantly short of the theoretical values. Particularly for direct carbonation, the efficiency could be as low as 0.5% and commonly remains below 30%[36]. Beyond their CCS potential, alkaline wastes usually contain appreciable quantities of valuable elements such as vanadium[50] and rare earth elements[51] and hence resource recovery or waste beneficiation would substantially promote the circular economy. In the case of indirect carbonation, an extraction step allows for nearly 100% utilisation of calcium/magnesium for CCS[52] and the wastewater could be further treated to recover other valuable elements[53]. Additionally, reagents can be recirculated or recycled to maximise their reaction efficiency[54].

Direct carbonation, however, only converts the surface layer of the waste into carbonates, leaving a significant proportion of the waste's core unchanged. This poses several technical and environmental challenges to utilising such materials in sustainable cements: (i) hazardous elements may exhibit elevated leaching after carbonation[55], both during the process and within the cement matrices; (ii) impurities can affect the polymorphisms of calcium carbonate and their transformations during carbonation, storage and utilisation[31,45]; (iii) the carbonated layer may contain different elements from the raw wastes[15], with varying chemical and mineralogical compositions[56], that may interact with cement phases differently; and (iv) different sizes of the waste powders exhibit different carbonation degrees and the chemical/mineralogical heterogeneity[46] can result in different effects on the cement properties.

On the other hand, numerous research and application opportunities exist to enhance sustainability within the construction industry. These include but are not limited to (i) developing advanced in-situ analytical techniques to monitor the waste carbonation and cement hydration processes[57]; (ii) controlling the characteristics of the carbonation layer to improve the performance of cements; (iii) combining CCS, hazardous materials treatment and resource recovery as a low-carbon remediation technology[15]; and (iv) exploring the synergy between carbonated wastes and other supplementary cementitious materials for either better cement performance or higher efficiency of waste treatment. It is evident that addressing these challenges necessitates interdisciplinary collaborations and multiscale mechanistic studies to advance our scientific understanding of process chemistry, thermodynamics, reaction kinetics and mass transfer in different heterogeneous systems.

TOWARD LARGE-SCALE CCUS OF ALKALINE WASTES IN SUSTAINABLE CEMENTS

Despite numerous research efforts on CCUS of various types of alkaline wastes in cements, there remains a significant gap in implementing these practices at an industrial scale. Several key challenges and opportunities need to be addressed to bridge this gap. Firstly, the heterogeneity of the wastes introduces unpredictability in the carbonation process and the performance of the resulting products, making their utilisation a considerable challenge. Variations in the properties of carbonated wastes and subsequently the cement properties incorporating them have been extensively discussed in various review articles[58,59]. Secondly, much of the research is conducted under aggressive conditions with pure CO_2 gases to accelerate the carbonation rate. However, there is a lack of understanding regarding how alkaline wastes perform when exposed to industrial flue gases directly for carbonation. In this regard, Pan et al.[60] showed promising results by using basic oxygen furnace slag and cold-rolling wastewater to remove 96-99% CO_2 from the real flue gas from the steelmaking industry while producing calcite. Thirdly, cement standards are often proprietary and current standards do not permit the use of carbonated alkaline wastes directly in their compositions. Standardisation processes for the integration of new materials into cement and concrete should be expedited, particularly focusing on the development of performance-based standards[61] given the urgent need to reduce clinker content and lower the carbon footprint of cements. Large-scale demonstrations are critically needed to evaluate the real-world performance of these novel sustainable cements.

Recent successes of alkaline waste CCUS for sustainable cements are exemplified in China. In 2022, supported by Jiyuan China United Cement Co., LTD, researchers at Nanjing Tech University implemented the technology of treating steel slag fine powders with CO_2 to produce SCMs[62] at an industrial scale, utilising CO_2 directly from a cement plant's flue gas. This single project will result in the upcycling of 300 kilotons of steel slag, and the direct elimination of 16 kilotons of CO_2 emissions every year[63]. A parallel successful demonstration took place at Daye Jianfeng Cement Co., Ltd., where SCMs were produced through microbial synergy fixing CO_2 from flue gas in steel slag[64]. Such demonstrations are crucial for achieving widespread adoption and implementation of carbonated alkaline waste materials.

An additional opportunity is to explore various applications of these cements, including in geotechnical and geoenvironmental infrastructure, where performance-based standards are available and followed. Last but not least, there is a notable absence of holistic studies that encompass economic, technical and environmental assessments of CCUS of alkaline wastes in cements, which is key to advancing this technology. It is worth noting that some researchers have conducted life cycle assessments (LCAs) of carbonation of silicate rocks[65] and steel slags[66], showing negative

carbon emissions in these processes. However, for many other hazardous alkaline wastes, additional factors influencing the carbonation efficiency, energy and reagent consumption, cement properties and the potential environmental risks should be taken into consideration. Such analyses are crucial to ensure that the benefits of using carbonated alkaline wastes are not offset by unintended negative environmental consequences. Furthermore, demonstrating the additional economic and environmental benefits of utilising carbonated alkaline wastes can facilitate market acceptance of these materials beyond relying solely on the engineering performance of cements.

CONCLUSIONS AND OUTLOOK

The cement industry's significant global impact underscores the necessity and urgency of implementing clinker replacement as we strive to achieve net-zero emissions. CCUS of alkaline wastes in sustainable cements holds immense promise for the construction sector, yet it is not without significant challenges. To maximise the benefits of calcium carbonate derived from alkaline waste carbonation in sustainable cements, we have demonstrated that: (i) different forms of calcium carbonate exhibit distinct properties and they can be readily produced by adjusting the carbonation conditions and (ii) cement properties can be optimised by adjusting the content and type of the calcium carbonate as well as the cement composition. Nevertheless, the industrial-scale and real-world implementation of CCUS of different alkaline wastes in cements remains limited due to various challenges, including (i) a lack of comprehensive scientific understanding regarding how impurities in alkaline wastes and flue gases influence the carbonation process, the properties of carbonated products and ultimately cement performance; (ii) the absence of holistic and systemic assessments of the economic and environmental benefits and risks, taking into account CCS, resource recovery, waste treatment and variation in cement performance; and (iii) the slow standardisation process and lack of performance-based standards to facilitate large-scale demonstration and real-world applications of these novel cements containing carbonated alkaline wastes. Moreover, it should be noted that for cements used in concrete, CCUS may lead to lower pH of the pore solution that may undermine the durability of steel reinforcement[67], which warrants further studies.

However, given the pressing need to achieve net-zero emissions at global, national, local and industrial levels, we believe there are substantial opportunities to further explore and develop the CCUS technology with various types and large quantities of alkaline wastes available today and those expected to be generated in the future. To realise the true values of alkaline wastes in combating climate change, interdisciplinary research should be coordinated involving but not limited to chemists, materials scientists, civil and environmental engineers, and social scientists. Furthermore, it is imperative to establish strong links between academia, industry, regulatory bodies and governments to comprehensively assess the viability of the technology from different angles and under different scenarios in order to make real-world impacts on both local and global scales.

DATA AVAILABILITY

All data generated or analysed during this study are included in this published article.

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ACKNOWLEDGEMENTS

AUTHOR CONTRIBUTIONS

F.J. wrote the manuscript and M.Z., M.X., L.M. reviewed the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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