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42nd Annual Cement & Concrete Science Conference

Ian Richardson

11 - 12 SEPTEMBER 2023

42nd Cement and Concrete Science Conference
11-12 September 2023
Imperial College London, United Kingdom

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42nd Cement and Concrete Science Conference
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Welcome to Imperial College London

On behalf of the Conference Organising Committee and sponsors we welcome you to the 42nd Cement and Concrete Science Conference, held in the Department of Civil and Environmental Engineering at Imperial College London.

Cement and concrete materials continue to be used in massive quantities worldwide in many applications. Their extensive scale of use makes improving their technical and environmental performance important for sustainable development. They are also key drivers for innovation.

This conference received 61 abstracts covering a wide range of work in the cement and concrete science domain. The conference programme includes 25 oral presentations including four keynotes plus many additional poster presentations, spanning topics from cement hydration to environmental sustainability. We thank those who have contributed to the conference, particularly our four distinguished keynote speakers and the sponsoring organisations for their support.

The Cement and Concrete Science Conference series has always tried to encourage early career researchers to present their work, and this remains a central goal of the meeting. Our aim is to provide a friendly forum where academic researchers, students, and industrialists can meet to discuss recent scientific advances and novel applications in cement and concrete science. We also hope to foster the UK community working in this field.

We wish you have an interesting, stimulating, and enjoyable time during the conference and your stay in London.

The Conference Organising Committee

Conference Organisation

Conference Organising Committee

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Conference Programme

Start time	End time	Location	Agenda item
Sunday 10 September			
1600	2200	Skempton foyer	Registration
Monday 11 September			
0700	1000	Senior Common Room	Breakfast
0800		Skempton 060A-C	Registration opens
0900	1000	Skempton 060A-C	Registration and refreshments
SESSION 1 – KEYNOTES			
1000	1010	Skempton 164	**Introduction and welcome from the conference organisers** Rupert J. Myers, Imperial College London
1010	1015	Skempton 164	**Welcome from the Head of the Department of Civil and Environmental Engineering** Washington Y. Ochieng, Imperial College London
1015	1100	Skempton 164	**Keynote: Unfolding the potential of mechanochemical processes for innovative design of low-carbon materials** Xinyuan Ke, University of Bath
1100	1145	Skempton 164	**Keynote: Earthen materials in the time of concrete** Christopher Beckett, University of Edinburgh
1145	1200		Comfort break
SESSION 2 – NOVEL CEMENTITIOUS MATERIALS			
1200	1215	Skempton 164	**Developing circular concrete through acid leaching of waste fines** T. Ding, H. Wong, M. Yio, C. Cheeseman
1215	1230	Skempton 164	**Electric clinker** S. Joseph, R. Prajapati, J. Allwood, C. Dunant
1230	1300	Skempton 164	**Poster pitches**
1300	1430	Skempton 060A-C	Group photo, lunch, and poster session
SESSION 3 – MATERIAL PROCESSING AND ENVIRONMENTAL SUSTAINABILITY			
1430	1445	Skempton 164	**Towards low-carbon structural building designs: Analyzing embodied carbon in reinforced concrete members through sensitivity analysis and life cycle assessment** A. S. Younus, P. Purnell, H. Fang
1445	1500	Skempton 164	**PCM-biochar composites: Advancing energy efficiency in built environment** M. Katish, S. Allen, A. Squires, V. Ferrandiz-Mas
1500	1515	Skempton 164	**Comparative life cycle assessment of composite Portland cement incorporating bauxite residue** C. O. Kilcan, M. Georgiades, R. J. Myers, A. H. Tkaczyk
1515	1530	Skempton 164	**A sensitivity analysis on the upscaling of a novel bauxite residue vitrification technology: An ex-ante life cycle assessment case study** M. Georgiades, C. O. Kilcan, T. Hertel, M. Giels, A. H. Tkaczyk,

			C. Cheeseman, R. J. Myers
1530	1600	Skempton 060A-C	Coffee break and poster session
SESSION 4 – CONCRETE AND BRICKS			
1600	1615	Skempton 164	**Aerial additive manufacturing in construction using multiple autonomous drones** B. Dams, P. Shepherd, R. J. Ball
1615	1630	Skempton 164	**Is 3D concrete printing low carbon? Getting it right** A. Selvaratnam, M. Achintha
1630	1645	Skempton 164	**Developing a generalised complete data-frame using machine learning algorithms for predicting the mechanical properties of concrete mix-designs** E. H. Laskar, S. Boral, L. Black
1645	1700	Skempton 164	**The influence of microstructural characteristics on mechanical properties of laterite bricks stabilized with cement, rice husk ash and saw dust ash** A. Oladapo, O. L. Oke, O. M. N. Ogundipe
1700	1710	Skempton 164	**Close of day 1** Rupert J. Myers, Imperial College London
1710	1800	Skempton 164	IOM3 Cementitious Materials Committee AGM (invite only)
1900	2100	Sherfield Building, Senior Common Room	**The Conference Dinner**
2100	2400	Union Bar, Beit Quad	Delegates are encouraged to meet at Union Bar for informal socialisation
Tuesday 12 September			
0700	1000	Senior Common Room	Breakfast
0830	0900	Skempton 060A-C	Refreshments
SESSION 5 – KEYNOTES			
0900	0945	Skempton 164	**Keynote: Cement industry landscape – challenges & responses** Nina Cardinal, Hanson Cement
0945	1030	Skempton 164	**Keynote: Potential improvements in cement sustainability: 2011-2023** Christopher Cheeseman, Imperial College London
1030	1100	Skempton 060A-C	Coffee break and poster session
SESSION 6 – CEMENT HYDRATION			
1100	1115	Skempton 164	**Analysis of William Aspdin's 1850 hardened cement paste: Compositional and microstructural examination** A. B. Owusu, I. G. Richardson
1115	1130	Skempton 164	**Fabrication of novel aerated concrete blocks by combining traditional and synthetic materials** Madhumita Biswas, Ashok N. Bhaskarwar
1130	1145	Skempton 164	**Reclaimed calcined clays: A new generation of UK supplementary cementitious materials for low carbon concrete** C. McCague, R. Griffiths, D. Casey, Y. Cao, Y. Wang, Y. Bai, T. Hope, M. Newlands, M. McCarthy, R. Jones, B. Benevenuti, D.

			Ansari, A. Smith, L. Wachter, S. Chudley, N. Cardinal
1145	1200	Skempton 164	**Suitability of thermally activated Yorkshire clays as supplementary cementitious material** S. A. Rahmon, Y. Dhandapani, S. Krishnan, A. T.M. Marsh, F. Kanavaris, L. Black, S. A. Bernal
1200	1330	Skempton 060A-C	Lunch and poster session
SESSION 7 – NUCLEAR AND ALKALI-ACTIVATION			
1330	1345	Skempton 164	**Replacement of Portland cement (PC) with hardened cement paste (HCP) treated with acetic acid and sodium carbonate aiming for cementation of nuclear wastes** A. K. B. Zahari, S. R. Yahaya, H. Kinoshita
1345	1400	Skempton 164	**Understanding cement-superplasticiser interactions in blended Portland cement wasteforms - blast furnace slag blends formulated with a polycarboxylate ether superplasticiser** A. Sjoberg, D. A. Geddes, J. L. Provis, G. M. Cann, B. Walkley
1400	1415	Skempton 164	**Synthesis of one-part geopolymers from alkali-mechanochemically activated clay minerals** V. A. Baki, X. Ke, A. Heath, C. Terzi, S. A Bernal, J. Calabria-Holley
1415	1430	Skempton 164	**Characterisation of calcined waste clays and utilisation in alkali-activated blends with GGBFS** L. Stefanini, D. Ansari, B. Walkley, J. L. Provis
1430	1500	Skempton 164	Coffee break and poster session
SESSION 8 – DURABILITY AND THERMODYNAMICS			
1500	1515	Skempton 164	**A phase-field-based chemo-mechanical model for corrosion-induced cracking in reinforced concrete** E. Korec, H. S. Wong, M. Jirasek, E. Martinez-Paneda
1515	1530	Skempton 164	**Accelerated weathering testing of ACMU composed of free mica and pyrrhotite-bearing phyllite from Co. Donegal, Republic of Ireland: Initial evaluation & deterioration discussion** B. Staniforth, C. Garner, C. Brough, J. Strongman, J. Fletcher, R. Garside
1530	1545	Skempton 164	**Evaluating thermodynamic constants of iron-containing siliceous hydrogarnet** B. Zhan, A. Baral, T. Hanein
1545	1600	Skempton 164	**Award of prizes, closing remarks** Rupert J. Myers, Imperial College London

Extended Abstracts: Keynotes

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UNFOLDING THE POTENTIAL OF MECHANOCHEMICAL PROCESSES FOR INNOVATIVE DESIGN OF LOW-CARBON MATERIALS

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ABSTRACT

Mechanochemical synthesis and activation is an emerging chemical route that uses mechanical energy supplied by electricity to induce chemical reactions, which might require high temperature and/or pressure conditions to take place. Apart from the physical changes, such as particle size reduction, and surface fractures, caused by the mechanical grinding processes, the mechanochemical process leads to chemical changes in materials, breaking and creating new chemical bonds and modifying chemical properties on the surfaces of the solids. The effectiveness of the mechanochemical activation processes is determined by the activation energy required for inducing the targeting reactions, and the impact energy created by the selected milling parameters, including the ball-to-sample mass charge ratios, milling time, and hitting frequencies. This energy can induce surface modification on minerals and carbonates of the material, reduce their crystallinity, and lower the binding energy of the surface chemical bonds.

As an emerging technology, the mechanochemical processes have been used in the construction industry for the development of novel low-carbon materials. The mechanochemical/mechanical activation method has been used for improving the reactivity of clay minerals, and alkaline solid wastes, as supplementary cementitious materials. Increased carbon dioxide absorption capacity from the atmosphere has been observed in these mechanochemically treated clay and mineral materials. At the same time, improved mineral carbonation capacity of calcium and/or magnesium silicate minerals, as well as inorganic solid waste materials, such as red mud and mine waste were reported after mechanochemical activation treatment. This presentation discusses the state-of-the-art of mechanochemical activation technology and its potential to be used in the construction industry for the innovative design of sustainable low-carbon materials.

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EARTHEN MATERIALS IN THE TIME OF CONCRETE

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ABSTRACT

Earthen materials are those that comprise unfired soil as their primary component. In their basic form, they rely on the combined effects of friction between the particles and the binding action of microscopic water menisci to maintain their mechanical properties. As such, earthen materials are particularly vulnerable to damage due to water ingress. A structure's earthen components can be protected by isolating them from the various exposure routes to water but this limits the structure's architectural and functional flexibility. Most traditional earthen walls that were exposed to the weather, for example sections of the Great Wall of China, were therefore stabilised with chemical (lime, ash) or biological additives (blood, manure, milk, plant oils/gums). Modern earthen construction predominantly includes cementitious agents (including alkali-activated materials), due to their availability, which has increased the range of soils that can be used for earthen construction but at the cost of higher embodied carbon.

Academic research into earthen materials has increased exponentially over the past two decades due to their perceived environmental and sustainable qualities. This keynote lecture will discuss work which we and others have done to understand how different stabilisers interact with the soil in earthen materials and, subsequently, to characterise their hydromechanical behaviour. Critically, we will explore two aspects that separate earthen material behaviour from the more familiar Civil Engineering materials of brick and concrete: microstructure; and suction. The lecture will discuss our progress to formalise this understanding through international standards, the opportunities that earthen materials afford us for low-energy living, and highlight those areas desperate for research in the stabilised earthen material sphere.

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POTENTIAL IMPROVEMENTS IN CEMENT SUSTAINABILITY: 2011-2023

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ABSTRACT

This conference was last held at Imperial back in 2011. One of the keynote lectures at that event was given by Gartner on potential improvements in cement sustainability. Gartner was well-known and highly respected within the cement and concrete science community and cement sustainability continues to be a critically important subject for both academic research and the industry. It is therefore interesting to review the Gartner paper from 2011 and assess the status of the five key alternative binder systems that were proposed and expected to have significant impact. The reasons why some of these have not developed as expected will be outlined. In comparison, the technologies that are currently contributing to improved cement sustainability will be reviewed. The industry is expecting carbon capture at cement plants to have the major contribution to reducing future carbon emissions. However, technologies using engineered supplementary cementitious materials (SCMs) are also expected to have a key role. These include the use of LC3 cements, particularly in developing countries, and SCM production from concrete extracted from construction and demolition waste. This also has potential to allow the development of circular concrete. Recent research using magnesium silicate minerals to manufacture a low-carbon amorphous precipitated silica SCM, and magnesium carbonate construction products will also be reviewed. The potential impacts of this technology on achieving sustainable cement will be discussed.

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CEMENT INDUSTRY LANDSCAPE – CHALLENGES & REPSONSES

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ABSTRACT

Due to the climate change crisis, the cement industry is undergoing unprecedented change. After providing a short overview to the UK cement industry and outlining its climate change and resource challenges, this keynote lecture focuses on developments taking place to decarbonise the industry. The UK Cement and Concrete Industry Roadmap outlines five areas for CO_2 reduction, ranging from the Scope 2 and 3 emission reductions associated with transport and electricity to the development of low carbon cements and concretes, alternative fuel options and carbon capture, usage and storage. The role of multicomponent cements with their imminent introduction into the UK regulatory framework is explained, as are developments with regards to calcined clays and the potential of recycled concrete fines. On the process side, trends in the use of alternative fuels and raw materials are explored, before moving onto the topic of carbon capture and storage, providing an insight into the most advanced development of a carbon capture project associated with a UK cement kiln. The lecture concludes with the role of standardisation and industry-academia collaboration in the ongoing efforts to decarbonise the cement industry.

Extended Abstracts: Oral Presentations

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DEVELOPING CIRCULAR CONCRETE THROUGH ACID LEACHING OF WASTE FINES

Tiejun Ding [a,1,^], Hong Wong [a,2], Marcus Yio [a,3], Chris Cheeseman [a,4,*]
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ABSTRACT

Concrete recycling primarily produces low-grade recycled concrete aggregates with reduced properties. Additionally, the recycling process generates a fine powder (< 0.15 mm) where most old cement paste accumulates. This adversely affect the performance of concrete and is unsuitable for reuse. Using SCMs to replace some cement is effective in reducing the carbon emission in construction. Commonly used SCMs are produced through energy-intensive and carbon positive processes and probably less available because these industrial processes are moving to more sustainable practices. Developing new SCMs with large availability and high quality has become an important research focus.

Indirect carbonation has been shown to improve the value of waste concrete fines. This method includes dissolving the hydrated cement paste using acid and sequestering CO_2 using the resulting Ca^{2+}-rich solution. Acetic acid (CH_3COOH) has been widely used because its safety and lack of Cl^- and SO_4^{2-} which have adverse effects on concrete durability. After acid leaching, the properties of the recycled aggregates are improved, making them suitable for reusing in new concrete. CO_2 sequestration using the Ca^{2+}-rich solution reduces the carbon footprint of the concrete and generates precipitated calcium carbonate (PCC) which can also be reused in concrete. This process has significant potential to achieve circular concrete. However, few studies have examined the silica-rich solid residue generated from this process. More detailed evaluations are required to understand its characterisation, reactivity and impact on mortar strength. Also, it is necessary to assess the applicability of this technology to waste concrete fine powder to make all components of concrete circular. Waste concrete fine powder from actual recycling facilities has a complex mineral composition because of contamination, so finely ground hydrated cement paste is used as the synthetic waste powder. The objectives of this work are to optimise process variables to maximise Ca^{2+} extraction, to compare the silica-rich residue generated from actual waste concrete fines and hydrated cement paste, to assess the potential for these materials to be used as an SCM by investigating their effect on the strength of cement mortars and to investigate the production of PCC through carbonation of the Ca^{2+}-rich solution.

Acetic acid leaching of hydrated cement paste has been done with various acid concentration, liquid/solid (L/S) ratio, temperature and time. The silica-rich solid residue from waste concrete fines (SR1) is prepared according to the optimised process in our previous work. The solid residue from hydrated cement paste (SR2) is produced under the optimal leaching conditions found in this work. The pozzolanic reactivity is tested using the R^3 method specified in ASTM 1897-20. The compressive strength test follows British Standard BS 3892-1-1997. The pH of the Ca^{2+} rich leachate is adjusted to 10.5 by adding concentrated ammonia solution ($NH_3 \cdot H_2O$). The impurities are removed by vacuum filtration. Then the solution was carbonated with pure CO_2 to produce $CaCO_3$.

The optimal leaching conditions for hydrated cement paste are an acid concentration, L/S ratio, temperature and time of 2 mol/L, 12.5 mL/g, 60 °C and 1 hour, respectively. The aluminosilicate SCM has significant pozzolanic reactivity, comparable to silica fume and fly ash. The reactivity of SR1 is lower than SR2 but is sufficient for compressive strength contributions. High-purity vaterite can be produced through CO_2 sequestration using the Ca-rich leachate and this can be used as a low-carbon binder. This study has proposed a novel aluminosilicate SCM and low-carbon binder from acetic acid recycling process for waste concrete fines to produce sustainable circular concrete and reduce emissions from concrete production processes.

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ELECTRIC CLINKER

Shiju Joseph [a,1,^], Rohit Prajapati [a,2], Julian Allwood [a,3] and Cyrille Dunant [a,4,*]
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ABSTRACT

The production of Portland cement clinker is a major contributor to global CO_2 emissions, with approximately 60% of these emissions coming from the decarbonization of limestone. To abate these emissions, most limestone could be replaced with decarbonated sources of calcium, such as recovered cement paste or metallurgical slags. The remaining 40% of CO_2 emissions originate from the combustion of fossil fuels. These emissions can be significantly reduced and potentially eliminated altogether with a decarbonized grid, by electrifying the heating process. Electric arc furnaces or induction furnaces can produce clinker electrically, with the heat source being the molten steel itself. After the clinker is formed and tapped off for cooling, the molten steel could remain within the furnace eliminating the need for remelting/reheating steel. In the present study, clinker was produced at around 1600-1700 °C in an induction furnace using different proportions and combinations of lime, kaolin clay, silica sand, hydrated cement paste and recovered cement paste from CDW. Two different induction furnaces were. One had a graphite crucible while the other used a MgO crucible with 1:3 and 1:6 flux to steel ratio respectively. The clinkers produced exhibited a broad range of compositions, with alite content ranging from 24% to 73%, belite from 9% to 60%, and tricalcium aluminate from 9% to 40% (Fig. 1). This indicates the versatility of the process in generating various clinker mineralogies. Fig. 2 shows the isothermal calorimetry performed on selected clinkers ground in a lab-scale ball mill and blended with gypsum. The results show high reactivity on par or higher compared to commercial clinker. This opens a way for the commercial production of clinker at scale using electricity. Although the energy demand will be more due to the higher temperature of clinker, the heating process, by contact over molten steel, will be more efficient than in a conventional kiln. The main heat loss will occur during the taping of clinker and this heat could likely be almost fully recovered. We expect this electrical process to approach the theoretical demand of 1.8GJ/t of clinker as opposed to 2.5GJ/t which is typical for best in class of fossil fuel kilns or 5-7GJ/t using hydrogen from electrolysis. The use of a decarbonated source of calcium could further reduce the energy requirement as decarbonation of limestone requires 1.8GJ/t of energy without considering other losses

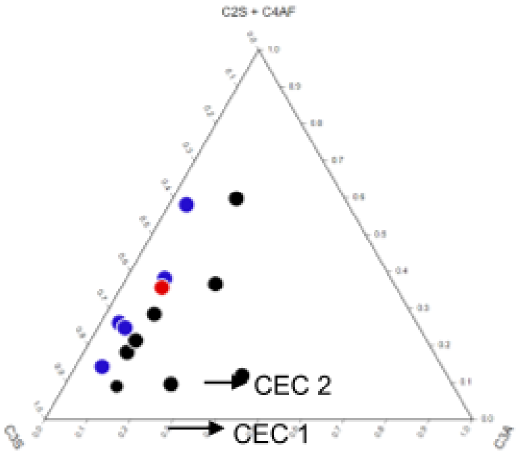

Figure 1: Plot of the composition of the clinkers produced. Red: Commercial clinker, black: graphite crucible, blue: MgO crucible

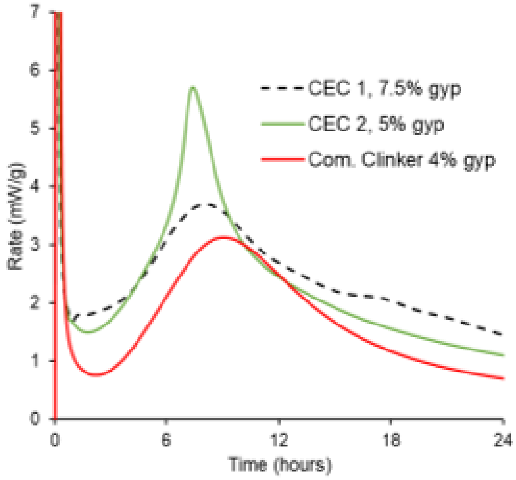

Figure 2: Isothermal calorimetry results of selected clinkers blended with gypsum

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TOWARDS LOW-CARBON STRUCTURAL BUILDING DESIGNS: ANALYSING EMBODIED CARBON IN REINFORCED CONCRETE MEMBERS THROUGH SENSITIVITY ANALYSIS AND LIFE CYCLE ASSESSMENT

Ahmed Sameer Younus [a,1,^], Phil Purnell [a], Han Fang [a]
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^ Presenting author. *Corresponding author. Email: cnasy@leeds.ac.uk

ABSTRACT

The construction industry's significant role in global materials consumption, associated with high embodied energy and carbon emissions, necessitates immediate action towards low-carbon building designs. The embodied carbon of reinforced concrete (RC) members is affected by various structural design factors, such as concrete strength, applied load, member geometry, steel reinforcement ratio, etc.

To achieve low-carbon RC structures that move us towards net-zero emissions, this research introduces equations derived from RC building design codes that correlate structural design parameters with the resulting embodied carbon emissions for RC beams, suggesting design interventions that could reduce their total carbon emissions.

The study shows that in terms of reducing carbon emissions, RC beam design factors can be divided into two categories: The first category includes variables such as cross-sectional width over depth ratio (b/d), steel reinforcement ratio, yield strength of steel reinforcements, and compressive strength of concrete, which affect carbon emissions regardless of their interaction with other building components. i.e., analysis is performed at the component level.

The second category includes parameters such as beam length and applied load. This can be optimised to generate more effective reductions in carbon emissions. However, their impact depends on the beam's interaction with other building components. i.e., analysis is performed at the building level.

It was found that in the first category, the steel reinforcement ratio and (b/d) ratio have the greatest impact on embodied carbon, while the beam's length has the most significant impact in the second category.

This research is part of a broader project aiming to reduce embodied carbon in RC structures through the optimisation of early design decisions, starting at the member level and progressing to the whole building structural system. The approach combines sensitivity analysis with Building Information Modelling (BIM) and Life Cycle Assessment (LCA) to identify critical design variables influencing a building's environmental performance throughout its life cycle.

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PCM-BIOCHAR COMPOSITES: ADVANCING ENERGY EFFICIENCY IN BUILT ENVIRONMENT

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ABSTRACT

In the context of the built environment, where a significant portion of global CO_2 emissions (approximately 40%) stems from high energy consumption for space heating and cooling, there exists a crucial opportunity to address this issue through energy-saving measures. One effective approach involves enhancing the thermal energy storage capabilities of building structures. Phase change materials (PCMs) possess the unique ability to absorb and release heat at specific temperatures, making them valuable for this purpose. However, challenges such as compatibility with building materials and potential leakage have hindered their widespread application.

To overcome these obstacles, a cost-effective solution has been developed: the formation of PCM-Biochar composites, which can be seamlessly integrated into concrete. This innovative method significantly improves compatibility between PCM and building materials, resulting in composites with exceptional thermal storage and insulation capabilities surpassing those of conventional alternatives. Octadecane and hexadecane were tested as PCMs, while pinecone biochar was selected as the ideal biochar for the mixture. The combination of PCM and biochar enables the production of a concrete mix with high latent heat capacity (See figure 1), facilitating efficient storage and release of thermal energy, precise temperature control, and reduced CO_2 emissions by minimising energy consumption. Moreover, the use of biochar represents a sustainable approach that reduces waste, as it can be obtained as a by-product of biomass fuel usage or through the incineration of forestry and agricultural residues.

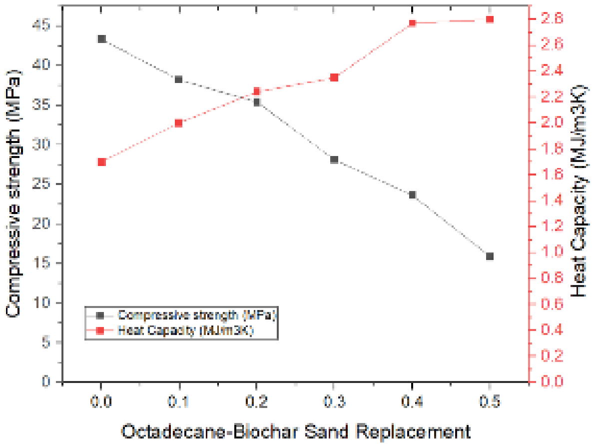

Figure 1: Heat Capacity vs octadecane-biochar sand replacement

Figure 2: Cross Section cut of PCM-Mortar at different ratios

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COMPARATIVE LIFE CYCLE ASSESSMENT OF COMPOSITE PORTLAND CEMENT INCORPORATING BAUXITE RESIDUE

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ABSTRACT

Great global benefits can be obtained by decreasing the cumulative environmental burden throughout concrete's life cycle due to its estimated annual worldwide consumption of ca 30 billion tonnes. The contribution of cement to this environmental burden is significant, since CO2 is emitted from limestone decomposition, and clinkerisation occurs under high temperatures (1400-1450 °C). Bauxite residue (BR) is a by-product of the aluminium industry with an estimated annual generation rate of ca 170 million tonnes and has the potential to be recycled as a supplementary cementitious material (SCM). This study explores the changes in various environmental impacts that may be expected when BR is used as a potentially low-impact substitute for clinker.
A comparative cradle-to-gate life cycle assessment (LCA) model was developed in Activity Browser software version 2.8.0, based on a functional unit of 1 m3 of concrete structure. BR-based composite Portland cements were compared with Portland composite cement – CEM II/A-M (0.2 wt% natural pozzolans, 1.3 wt% fly ash, 4.6 wt% granulated slag as SCMs) on the basis of equivalent functional performance in concrete. The BR- based cements contain 30 wt% treated BR. The comparison was performed based on the ReCiPe life cycle impact assessment method involving 18 impact categories assessed at midpoint level and using the hierarchist perspective. Two types of BR were considered: (i) BR co-calcined with kaolinite (at 750 °C) and (ii) vitrified BR (at 1200- 1300 °C). The region of concrete production is Europe, which is the geographical region selected for the background processes such as electricity generation, heat production, and transportation in the Ecoinvent database version 3.9.1. The results show that burden shifting in the concrete life cycle occurs in some impact categories due to use of BR-based cements instead of CEM II/A-M. The burden shifting arises from the BR treatment processes, despite several impacts showing considerable reductions (Figure 1). For example, compared to CEM II/A-M concrete, the global warming potential (kg CO2-eq m-3) of the BR-based concretes changes by - 17.7% in the co-calcination case, and - 12.0% in the vitrification case. However, the change is +2.5% (co-calcined BR-based concrete), and +45.9% (vitrified BR-based concrete) for the ionising radiation potential (kg Co-60-eq m-3), which reveals that artificial radioactivity elevates due to emissions from BR treatment. In this regard, at the unit process level, the highest contribution (~93%) to the ionising radiation potential stems from the share of nuclear power generation in the chosen electricity mix, more specifically emissions due to treatment of the uranium milling tailings. Thus, to avoid burden shifting in ionising radiation potential impacts, BR could be treated in regions where there is less nuclear energy and more renewable energy. Also, other strategies can be chosen to mitigate burden shifting in other impact categories, e.g., water consumption potential (WCP).

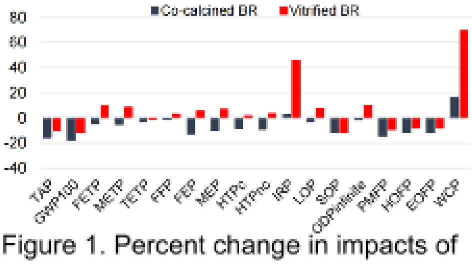

Figure 1. Percent change in impacts of concrete involving treated BRs relative to CEM II/A-M, based on Recipe Midpoint (H) LCIA method

The research leading to these results was performed within the ReActiv project and received funding from the European Union Horizon 2020 Programme (H2020/2014-2020) under grant agreement n°958208. Uku Andreas Reigo is thanked for his contributions. References: Monteiro, P. J. M., Miller, S. A., & Horvath, A. (2017). *Nature Materials*, 16(7). Amanor-Wilks, A. (2022). *IAI Releases Updated Sustainable Bauxite Residue Management* Guidance. https://international-aluminium.org/iaireleases-updated-sustainable-bauxiteresidue-management-guidance/

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A SENSITIVITY ANALYSIS ON THE UPSCALING OF A NOVEL BAUXITE RESIDUE VITRIFICATION TECHNOLOGY: AN EX-ANTE LIFE CYCLE ASSESSMENT CASE STUDY

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ABSTRACT

Cement production continues to be a major contributor to global CO_2 emissions, primarily emerging from the clinkerisation of limestone and fossil-based fuel mix. Significant efforts are being directed towards mitigating these emissions through well-established and emerging measures including the adoption of alternative fuels, carbon capture and storage, alternative raw materials, and supplementary cementitious materials (SCMs). An example of such emerging technology is the vitrification of bauxite residue (BR) as an SCM, but due to the relatively low technology readiness level (TRL) of this technology, assessing its environmental impacts at an industrial scale is challenging. This study focuses on evaluating the environmental performance of BR vitrification as an exemplar of emerging low carbon cement technology, by examining across different scales and data-upscaling approaches.

An ex-ante, cradle-to-gate, life cycle assessment was performed in Activity Browser 2.8 based on a functional unit of 1 kg of treated BR suitable as an SCM in blended cement. The environmental performance of the vitrification technology was evaluated at laboratory, pilot and industrial scale. Upscaling to the industrial level was performed by considering multiple approaches i.e., proxy technology, regression analysis, thermodynamic software, and process modelling. Six industrial scale scenarios were developed: (1-2) proxy technology – ceramic tile production (using two different inventory data sources i.e., 1 - BREF, and 2 - Ecoinvent 3.9.1), (3-4) regression analysis (power and linear), (5) thermodynamic calculations, (6) process modelling. Background processes were modelled based on Ecoinvent (v.3.9.1) assuming a European geographical context.

Results showed improvements in all impact categories during upscaling from laboratory to pilot (between ~74-92%) and from laboratory to industrial scale (~88-100%) (Figure 1). This result highlights the significant influence of upscaling on improving process efficiency and hence the substantial impact reduction. Comparing the industrial scale results shows a small variance in all impacts categories. For instance, a respective reduction in the global warming potential (GWP100) was found across the up-scaled scenarios i.e., 92% (proxy technology 1), 88% (proxy technology 2), 92% (power regression), 92% (linear regression), 91% (thermodynamic calculations), and 94% (process simulation). This result suggests that all the upscaling approaches studied here are applicable for early-stage assessment of emerging low carbon cement technologies.

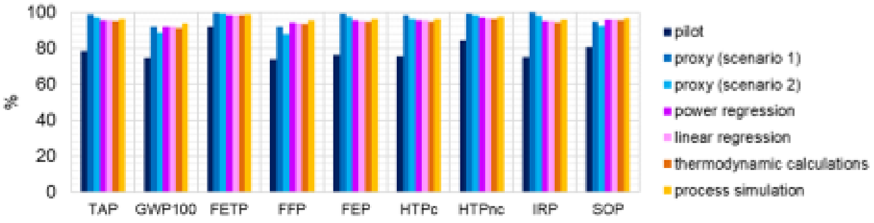

Figure 3: Percentage improvements in impact categories of vitrified BR from laboratory to pilot and laboratory to industrial scale for the six scenarios studied.

The research leading to these results was performed within the ReActiv project and received funding from the European Community's Horizon 2020 Programme (H2020/2014-2020) under grant agreement n°958208. References: Tsalidis, G. A., & Korevaar, G. (2022). *Resources, Conservation and Recycling*, 176. United Nations (UN). (2017). World Population Prospects Data Booklet 2017.

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AERIAL ADDITIVE MANUFACTURING IN CONSTRUCTION USING MULTIPLE AUTONOMOUS DRONES

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ABSTRACT

Additive manufacturing, better known as '3D printing' is being increasingly investigated as a method of constructing buildings. Typically, deposition platforms involve large ground-based gantries or robotic arms. Aerial Additive manufacturing is the world's first to demonstrate the feasibility of multiple self-powered untethered drones extruding material in flight to construct multiple layers. Use of drones requires the miniaturisation of the additive manufacturing process and the use of lightweight cementitious material. Material in the fresh state needs to be pseudoplastic – exhibit shear thinning behaviour - reducing viscosity while the material is under stress in the deposition system, and increasing by orders of magnitude once deposited to minimise deformation due to subsequently deposited layers. Cellulose and xanthan gum were used as rheology modifying admixtures to promote pseudoplastic behaviour, with fly ash and smooth-particle sand used to aid workability. Typical material properties were a cured compressive strength of 25 MPa, a complex modulus of 4-9 MPa within a two-hour open time, a yield stress of 1.1 KPa and material densities of approximately 1650 kg/m^3. Material extrusion during autonomous flight is demonstrated with a printed 28-layer object. Aerial additive manufacturing could enable work in elevated or challenging site conditions and promote architectural freedom in design.

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DEVELOPING A GENERALISED COMPLETE DATA-FRAME USING MACHINE LEARNING ALGORITHMS FOR PREDICTING THE MECHANICAL PROPERTIES OF CONCRETE MIX-DESIGNS

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ABSTRACT

The twofold challenges of achieving Net Zero while shifting from a linear to a circular economy in the construction sector are driving the increased use of recycled materials. Current standards allow the use of 20% of recycled concrete aggregate (RCA), without minimal effect on mechanical performance. However, a holistic view is needed, considering environmental, economic and social aspects. Furthermore, there are a multitude of factors affecting concrete performance, e.g., strength, workability,RCA replacement percentage, etc.

Here, we have constructed a concrete mix- design database, considering 674 concrete mix designs, 84 explanatory variables and 7 response variables. In this initial analysis, we elucidate through descriptive statistical analysis the variations in 28-day compressive strength (MPa), cost (£/m^3), and carbon footprint (KgCO$_2$/m^3) as a function of RCA replacement percentage.
Using previously published literature, we collated a data-frame of 1500 samples. After careful data pre-processing (datacleaning, duplicate removals, samples with infeasible information), we included 674 final cases for analysis. Out 91 variables, only 24 had complete data, with the missing data for the others constituting between 1% and 94%. However, before performing multiple imputations through different machine learning approaches (to obtain a complete data-frame) and to compare results from available and imputed data, an initial observation of the patterns and statistical indices of the available data was required. Here we present three selected response variables according to grouped RCA replacement ratios. Each group and its respective response variables showed different trends, i.e. does not follow a single type of statistical distribution. This prevented a single type of normalisation approach (viz., max- min normalisation, robust normalisation, etc.) , which is a prerequisite before employing any machine learning model. Thus, in Figure 1, we presented the mean values of 28-days compressive strength, carbon footprint, and cost for different replacement percentages.

With increasing RCA replacement percentage, there was a decrease in mean compressive strength. This is due to the presence of adhered mortar on the RCA. The lower cost of RCA compared to natural aggregate meant that the cost also decreased. However, the slightly higher carbon footprint of RCA led to a slight increase in the resultant carbon footprint of the concrete. This throws up potential concerns with regards to meeting the twin goals of net zero and a circular economy. Following this initial work, machine learning approaches are being developed to better understand which factors most affect concrete performance when using RCA. This should help to promote more effective use of RCA in concrete.

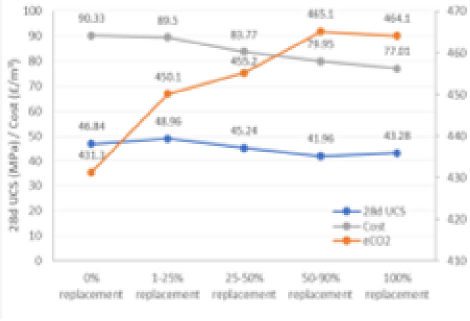

Figure 1. Variations in mean values of the response variables

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ANALYSIS OF WILLIAM ASPDIN'S 1848 HARDENED CEMENT PASTE: COMPOSITIONAL AND MICROSTRUCTURAL ANALYSIS

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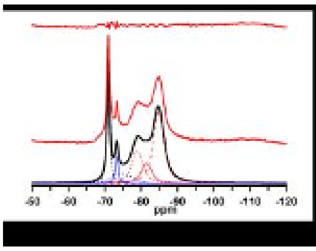
ABSTRACT

The analysis of old hardened cement samples offers unique opportunities to understand the evolution of cement and hydration products, particularly calcium silicate hydrate, which is the primary binding phase in Portland-based cement systems. This study aims to characterize a 175-year-old hardened Portland cement paste using various analytical techniques including NMR, XRD, SEM & TEM. The results obtained so far reveal a partially reacted Portland cement that had exceptionally large particles and C-S-H with very long aluminosilicate chains, both of which are consistent with the paste's age. The presence of hydrogarnet, an OH-AFm Friedel's Salt solid solution and other crystalline phases are discussed.

Sample: The sample is from a folly that is attached to a public house in Sheerness, Kent, UK (Historic England, List Entry 1273263). A ship's cargo of Portland cement in barrels from William Aspdin's cement works had washed up on the coast of Kent in 1848; the barrels had been soaked with sea water and the cement had set to form barrel-shaped blocks that were used to build the folly's walls.

Results: Figure 1 shows the single pulse ^{29}Si MAS NMR spectrum along with the deconvoluted peaks. The peaks have been assigned to various silicate structural units based on their distinct resonances. Q^1 identified at -78.9 ppm are end-chain units, Q^2 at -84.8 ppm are middle-chain units, and Q^2(1Al) at -81.5 ppm are middle-chain units with an adjacent tetrahedron occupied by aluminium. The two sharp peaks at -71 and -73.3 ppm are due to β-C_2S and γ-C_2S respectively (both Q^0). A small broad peak at about -75 ppm is assigned to Q^0(H), a hydrated monomer reported to be persistent during hydration [1]. However, it is likely that there is also some contribution from alite based on its observation in the BSE imaging. The calculated mean chain length (MCL) for the C-S-H is 8.1, which is much longer than values that have been observed for C-S-H present in younger pastes. XRD data confirms the presence of the anhydrous silicates indicated by the NMR results. The crystalline phases present include CH, AFt, β-C_2S, γ-C_2S, C_3S, C_3A, hydrogarnet, brownmillerite, quartz and a hydroxy AFm-Friedel's Salt solid solution. The presence of chloride ions in the sea water may have influenced the formation of this solid solution. BSE imaging of the sample reveals both hydrated and anhydrous materials in various sizes, with the largest measuring approximately 450 µm. The presence of exceptionally large cement particles is consistent with the age of the sample. Although partially hydrated large particles are abundant – e.g. as shown in Figure 2 – the presence of a significant number of smaller particles is revealed by relicts of fully-reacted calcium silicate phases. The Ca/Si atomic ratios (Table 1) calculated from SEM-EDX points selected on the basis of microstructural features indicate a high level of intermixture of C-S-H with other phases (including AFm) in both the Ip and Op regions.



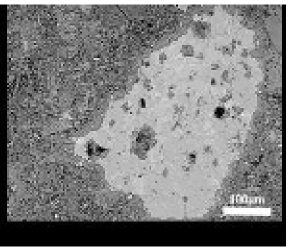


Table 1. Ca/Si ratio of Ip C-S-H, Op C-S-H and unhydrated material with standard deviation (SD) and number of analyses (N*)

	Ca/Si + SD	N*
Ip C-S-H	1.74 ± 0.10	354
Op C-S-H	2.08 ± 0.37	273

Conclusion: This study is focused on characterizing the composition and microstructure of a 175-year-old hardened cement paste. Anhydrous material is indicated by SEM, XRD and NMR results. The MCL of the C-S-H is very long. Results from SEM-EDX of Ip and Op suggest intermixture of C-S-H with other phases and so further analysis with TEM-EDX is required to determine its composition unambiguously.

References: [1] A.R. Brough, C.M. Dobson, I.G. Richardson, and G.W. Groves: *J. Mater. Sci.* 1994, 29, 3926 - 394

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FABRICATION OF NOVEL AERATED CONCRETE BLOCKS BY COMBINING TRADITIONAL AND SYNTHETIC MATERIALS

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ABSTRACT

The demand for green construction materials is growing worldwide for environmental protection reasons. The majority of CO2 emissions come from the concrete and construction sectors, which use natural resources for manufacturing. It also gives alarming notes on sustainability objectives. Since ancient times, the use of lime-based building materials has become popular. The lime mortar was prepared by mixing different natural additives (such as molasses, curdling, and egg yolk), which helps to gain strength as the lime mortar has less strength than the cement mortar but is more durable than the cement mortar. Many heritage monuments of the Indus Valley civilization made of lime mortar attest to the durability of lime-based structures. Lime-based mortar is still used in rural and suburban areas of India, along with other locally accessible reinforcing materials like rice husk and tree bark. Although the prepared building material is eco-friendly enough, it still has a higher dead weight and some durability issues (higher water absorption, etc.). Here, we discuss the surface treatment of the waste polyethylene bag cuts, which have a higher potential for littering, using the traditional building material lime (usually used as the main binding material). Thus, lime-coated polyethylene bag cuts were prepared. When those lime-coated polymeric wastes were employed in wet, aerated cement-based slurry, they offered higher performance in fibre-matrix bonding than that of the untreated polyethylene bag cuts. Additionally, we used an eco-friendly aeration technique that required less energy than the presently available aeration technique (i.e., an aluminium powder-based method). Colloidal gas aprons (CGAs), which are micron-sized bubbles, are introduced as an aerating medium in this novel technique.

The resultant aerated blocks possess low density, moderate [1.95–3 MPa] compressive strength, absorb less water, and are less prone to cracking due to the bridging effect of the plastic bag cuts. We were successful in using fly ash, another waste, during the preparation of the aerated slurry, which reduces the need for cement, the main binder, and lowers the carbon impact. Hence, by using waste materials, these innovative reinforced aerated blocks would be able to achieve sustainability while also improving the characteristics of aerated blocks.

Experimental work done-

Lime coated polyethylene bag cuts were prepared and used in the CGAs based aerated slurry for preparation of the aerated blocks. Characterization of the blocks are under process.

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SUITABILITY OF THERMALLY ACTIVATED YORKSHIRE CLAYS AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

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ABSTRACT

The utilization of supplementary cementitious materials (SCMs) such as calcined clays has become a pivotal strategy to reduce carbon emissions associated with cement and concrete. The use of clays is attractive due to their global abundance. However, a substantial amount of clay resources in the UK and in many parts of the world are low purity, i.e. <40% kaolinite content, containing other clay minerals which are intrinsically less reactive, and/or greater proportions of associated minerals. This study investigated three distinct clays sourced from various locations within the Yorkshire region, historically recognized as the birthplace of Portland cement. The codes for each clay, and their geological classifications, are: KS (glacial till), FC (glaciofluvial deposit), and TF (Lias Group clay). The objective was to assess these clays' viability for use as SCMs in low-carbon concrete applications within the UK.

The clays were calcined at 800°C for a residence period of 1 hour in a lab-scale muffle furnace. The mineralogy of the raw and calcined clays was characterised using thermogravimetry and X-ray diffraction. The raw clays' kaolinite content are in the range of 9-29%. R3 chemical reactivity tests as per ASTM C1897-20 confirmed that KS and FC clays were moderately reactive once calcined (>200 J/g of SCM), as shown in Figure 1. Meanwhile clay TF, which contained < 10% kaolinite, was unreactive after calcination at the conditions adopted.

Standard mortars (BS EN196-1:2016) were prepared by partial replacement of Ordinary Portland Cement (OPC) with 30% calcined clay to produce binary blends (B), and 30% calcined clay + 15% limestone to produce ternary blended cements (T). The mortar specimens' compressive strength were measured up to 90 days. These calcined clays exhibited promising performance as SCMs, despite their relatively low meta-kaolinite content - binary blends containing 30% calcined clays gained comparable strengths to Portland cement mortar by 90 days (Figure 2). All ternary blends attained >40 MPa by 90 days of curing. TF-B and TF-T developed comparable strengths to mortars made with the other calcined clays, despite the substantially lower meta-kaolinite content of calcined TF. The outcomes of these tests provide valuable insights into the potential of calcined Yorkshire clays as SCMs to produce low-carbon concretes. The findings reinforce the significance of low-purity clays for pursuing effective decarbonisation strategies in the cement and concrete industry.

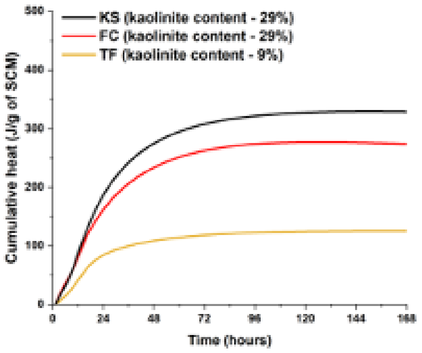

Figure 1: Cumulative heat released from R^3 test.

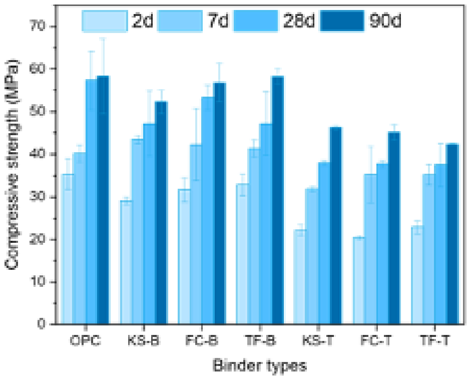

Figure 2: Compressive strength of OPC, binary (B) & ternary blended (T) mortars.

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REPLACEMENT OF PORTLAND CEMENT (PC) WITH HARDENED CEMENT PASTE (HCP) TREATED WITH ACETIC ACID AND SODIUM CARBONATE AIMING FOR CEMENTATION OF NUCLEAR WASTES

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ABSTRACT

Recycling of cement can reduce fresh cement use, thus reducing the associated CO_2 emissions deriving from its production. Recycled concrete fines (RCF) contain a significant amount of cement adhered to fine aggregates which often fall into disuse compared to its larger counterparts. Highly porous nature of RCF increases water demand when used in new cement paste. The present study aims the use of RCF for cementation of nuclear wastes whereby mechanical strength is not critical compared to structural applications. Pre-treatments of HCP were investigated, using two types of aqueous systems: acetic acid and sodium carbonate solutions. The HCP prepared in powder form (<250 μm) was treated by the corresponding solution and directly incorporated in the new cement system without separation. Cement with higher replacement of HCP pre-treated with sodium carbonate appear more difficult to mix than other samples suggesting lower workability. Inclusion of more HCP resulted in more reduction of compressive strength as expected. The impact of the strength reduction was smaller with the acetic acid pre-treatment, with the highest being 21.34 MPa at 20% HCP replacement while the lowest strength of 15.44 MPa was observed at the 40% HCP replacement with the sodium carbonate treatment, likely related to their pore structures (Figure 1a) and formation of the binding phase C-S-H (Figure 1b). Treatment mechanism of each solution is currently under investigation. Although reduced, the values are well above the 7 MPa threshold of the UK cement wasteform regulation requirement.

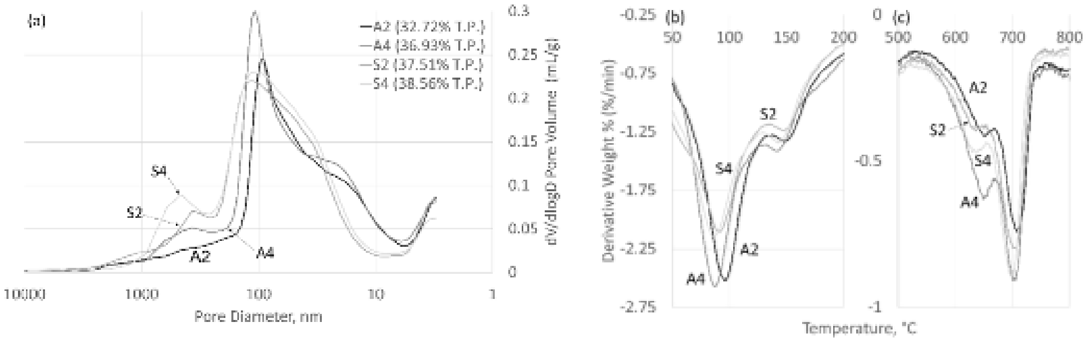

Figure 1: (a) Pore distribution using mercury intrusion porosimetry (MIP) method showing weaker 'S' samples (sodium carbonate treated) exhibit larger amount of macropores. (b) DTG data at 50-200°C showing higher amount of CSH present in stronger, 'A' samples (acetic acid). (c) DTG data at 500-800°C showing higher degree of carbonation reduces the overall pore size of the sample

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UNDERSTANDING CEMENT-SUPERPLASTICISER INTERACTIONS IN BLENDED PORTLAND CEMENT WASTEFORMS - BLAST FURNACE SLAG BLENDS FORMULATED WITH A POLYCARBOXYLATE ETHER SUPERPLASTICISER

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ABSTRACT

The addition of superplasticisers (SPs) and ground granulated blastfurnace slag (GGBS) to cementitious materials used for the encapsulation of radioactive waste will enable a more effective and sustainable immobilisation process. SPs reduce the water requirement of the grout while still achieving high fluidity by the dispersal of cement particles due to steric hindrance and electrostatic repulsion. There are many advantages of a low water-cement (w/c) mix with improved flow characteristics, such as an increased early strength, higher waste infiltration, and a less permeable cementitious matrix.

Supplementary cementitious materials such as GGBS can be introduced to Portland cement (PC) to function in conjunction with an SP by enhancing properties of the grout and reducing embodied CO_2 emissions. GGBS is used widely on waste encapsulation plants, however there is little understanding of what physicochemical parameters are critical to reliable performance.

This study investigates the interactions between PC particles, polycarboxylate-based SPs, and GGBS physiochemical properties such as surface charge, particle morphology, and particle size distribution vs.grout workability and flow characteristics, setting time, and rheological properties. This insight helps to reveal fundamental processes controlling dispersion and fluidisation in PC-GGBS grouts, providing better understanding of key parameters for robust specification.

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SYNTHESIS OF ONE-PART GEOPOLYMERS FROM ALKALI-MECHANOCHEMICALLY ACTIVATED CLAY MINERALS

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ABSTRACT

Geopolymers are promising clinker-free low-carbon cementitious materials that can effectively be produced using natural minerals or solid waste materials rich in poorly crystalline aluminosilicates. Despite the recent development of the design and synthesis of geopolymers, most of these materials have been prepared by a “two-part” method, requiring the use of highly alkaline solutions, which has brought challenges to real-life applications when considering materials transportation and on-site operations. One-part, sometimes also call as “just add water”, geopolymers have emerged as a potentially more convenient and operatable option, which could simplify the processes of handling alkali activator solutions. This study aimed to produce one-part "just add water" alkali-activated binders through alkali-mechanochemically activation. The mechanochemical activation of natural kaolinite clays with varying sodium hydroxide ratios results in changes in the physicochemical properties of kaolinite minerals, including specific surface area, chemical structure and leaching properties. The results also suggest that the hydration of one-part alkali-activated kaolinite mineral leads to the formation of zeolite A and alkali aluminosilicate hydrates (N-A-S-H) gels as the main reaction product. Hardened geopolymers developed a compressive strength results reach up to 11.5 after 28 days of curing. The outcomes from this study suggest that activating kaolinite minerals by mechanochemical activation with NaOH has great potential in developing novel one-part geopolymers.

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CHARACTERISATION OF CALCINED WASTE CLAYS AND UTILISATION IN ALKALI-ACTIVATED BLENDS WITH GGBFS

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ABSTRACT

The exploration of alternative materials for sustainable construction practices, predominately waste materials from industrial side streams, has gained significant scientific interest in recent years. This study investigates the potential of utilising industrial calcined waste clays of low purity, possessing low metakaolin content, as substitutes for ground granulated blast furnace slag (GGBFS) in alkali-activated cements (AACs) activated with sodium silicate.

Clay minerals, abundant and globally sourced, present a promising avenue for reducing the reliance on conventional construction materials and enhancing mechanical performance. The composition and microstructural properties of clays influence their suitability for certain applications. Calcined clays have already gained attention as supplementary cementitious materials (SCMs) due to their pozzolanic properties. Metakaolin, an anhydrous form of kaolinite, is a well characterised type of calcined clay, recognised for its consistent elemental composition and high pozzolanic reactivity. Waste calcined clays exist as a waste side stream from kaolinite extraction and calcination, usually containing stable mineral phases and residual metakaolin.

This study comprehensively characterises five calcined waste clays from Imerys (UK) and their behaviour in mixed AACs with commercially available GGBFS from Ecocem (Belgium). Physical attributes such as particle size, morphology, and phase composition are examined. The pozzolanic reactivity of calcined clays is also assessed. The research reveals that the R3 test assessing pozzolanicity is more indicative of clay behaviour in alkali-activated systems than the modified Chapelle test. However neither of these tests are sufficiently adequate to describe the reactivity of calcined clays in alkaline environments where calcium hydroxide is not present. The impact of calcined clays on fresh properties, especially workability, is notable, with clay morphology emerging as a significant factor in mix design and in influencing the physical characteristics of blended pastes. Adequate workability is crucial for generating well-performing binders with high strength, low porosity, and dense microstructures. By replacing up to 20 wt.% of GGBFS with calcined waste clay, comparable compressive strengths to traditional binders can be achieved, accompanied by an improvement in bulk density.

During first stages of alkali-activation, major mineral phases within the calcined clays: quartz, muscovite, and alkali-feldspars, remain chemically stable within the matrix and are not seen to participate in activation reactions. Conversely, the reaction of the amorphous phase fraction yields a more cross-linked C-A-S-H gel that enhances mechanical properties and reduces the porosity of binary binders. This study offers a holistic methodology for characterising waste clays and their behaviour in alkali-activated systems, fostering the design of novel binders that can incorporate significant fractions of waste clays. This approach aligns with general trend towards more sustainable construction practices with the valorisation of waste materials and inclusive formula optimisation to best achieve maximum mechanical strength in mixed GGBFS/waste systems.

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A PHASE-FIELD-BASED CHEMO-MECHANICAL MODEL FOR CORROSION-INDUCED CRACKING IN REINFORCED CONCRETE

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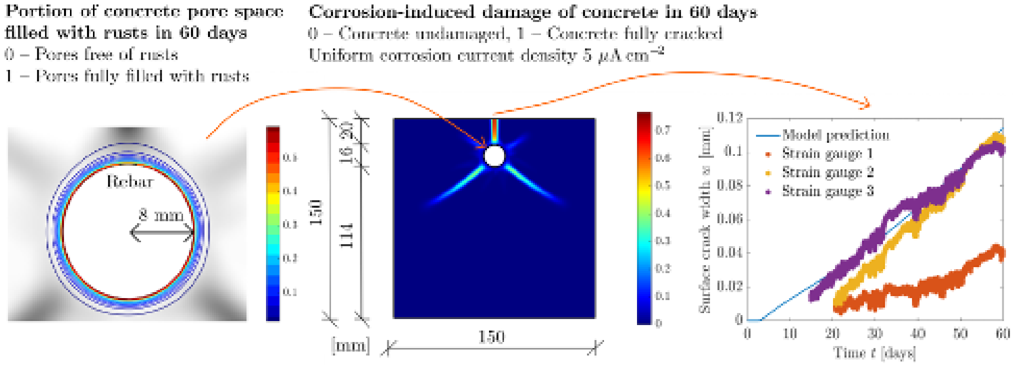
ABSTRACT

We present a new model [1] for corrosion-induced cracking in reinforced concrete. Corrosion-induced damage is practically important because it results in the delamination/spalling of concrete cover and is responsible for 70-90% of prematurely deteriorated reinforced concrete structures. The state-of-the-art knowledge of the involved chemo-mechanical processes was captured in several coupled parts of the model. Firstly, (A) the diffusion-driven reactive transport of iron ions from the corroding steel rebar and their precipitation into iron oxide and iron hydroxy-oxide rusts were simulated. The impact of the magnitude of the corrosion current density was taken into consideration which allowed for the comparison of the results obtained from the accelerated impressed current tests with those subjected to corrosion under natural conditions. A portion of rust forms the dense rust layer in the space vacated by steel corrosion while the remainder accumulates in the pore space of concrete. Also, the diffusion-driven transport of aggressive species triggering corrosion such as chlorides to concrete rebar from the external environment was considered. The enhanced transport of all involved species through cracks was resolved with the damage-dependent diffusivity tensor. Rust has a significantly lower density than original steel. Thus, the constrained accumulation of rust in the dense rust layer and concrete pores exerts pressure on concrete (B) which is predicted such that the mechanical properties of rust (Young's modulus and Poisson's ratio) were taken into consideration. A new precipitation eigenstrain concept was introduced to evaluate the corrosion-induced pressure of rust accumulating in concrete pore space. The quasi-brittle fracture of concrete was then simulated with the phase-field fracture model (C). The proposed model was implemented in COMSOL Multiphysics software and solved numerically with the finite element method. Both uniform and non-uniform corrosion case studies were investigated and validated revealing a good agreement with experimental data. The results also indicated that corrosion-induced fracture could proceed with a partial saturation of the concrete pore space with rust and rust was found to be spread even millimeters from the steel surface, reducing the precipitation-induced pressure and delaying cracking. In regions with locally nucleating cracks, dissolved iron species were preferentially transported deeper into the cracks and precipitated there or in areas away from the steel rebar. Also, the enhanced transport of chlorides through cracks was found to importantly affect the resulting steel mass loss and the surface crack width. The parametric study revealed the profound influence of the porosity of concrete and the mechanical properties of rust, specifically Young's modulus and Poisson's ratio, on the resulting surface crack width, highlighting the need for appropriate characterization studies of rust.



Portion of concrete pore space filled with rusts in 60 days
0 – Pores free of rusts
1 – Pores fully filled with rusts

Corrosion-induced damage of concrete in 60 days
0 – Concrete undamaged, 1 – Concrete fully cracked
Uniform corrosion current density 5 μA cm^{-2}

References: [1] E. Korec, M. Jirásek, H.S. Wong, E. Martínez-Pañeda, A phase-field chemo-mechanical model for corrosion-induced cracking in reinforced concrete, Construction and Building Materials. 393 (2023) 131964.

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ACCELERATED WEATHERING TESTING OF ACMU COMPOSED OF FREE MICA AND PYRRHOTITE-BEARING PHYLLITE FROM CO. DONEGAL, ROI: INITIAL EVALUATION & DETERIORATION DISCUSSION

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ABSTRACT

Widespread issues with deteriorating housing in Co. Donegal were first addressed around 2011 and were initially linked to the presence of excessive free mica in the binder of aggregate concrete masonry units (ACMU). Free mica was identified to be abraded from the muscovite-rich aggregate, a low-grade phyllite resulting in weakened cement binder susceptible to secondary processes. A compounding factor is the presence of pyrrhotite, a reactive iron sulphide highly susceptible to oxidation within the phyllite aggregate. Under appropriate conditions these ACMU can rapidly deteriorate, with concrete from affected dwellings currently being examined and classified by investigations in accordance with IS 465[1]. High potential for deterioration with pyrrhotite-bearing ACMU has been assessed and examples of deterioration by *in situ* oxidation have been examined by Petrolab and research organisations [2]. The aim of this study is to investigate the application of the RICS stage 3 (S3) expansion test [3] to a typical set of quarried phyllite ACMU from Co. Donegal, and thereby assess the potential for sulphate attack under controlled conditions. For this study, we utilised 10 core samples of ACMU taken as part of IS 465 scheme investigations. Samples exhibited between 6.8-20.6% voidage by modal analysis and a determined 6-14% free mica (<63 µm sized muscovite by cement). All but one sample was identified to comprise crushed phyllite aggregate originating from a single quarried source. S3 testing was undertaken in accordance with the RICS Mundic Guidance test method. Post examination observations were compared against baseline petrographic examinations and analysis which examined complete carbonation, limited sulphide oxidation, no sulphate replacement and very limited overall damage. All samples exhibited linear expansion below the 0.025% lower limit, with samples 001-007 & 010 exhibiting no undue linear expansion. Both 008 & 009 exhibited increasing linear expansion over the test duration, peaking at 0.0145% and 0.0165% maximum linear expansion but remained below the lower threshold. The total sulphur (TS) content of the phyllite blocks post-testing ranged between 0.38-0.80% (TS as S). These values are all significantly above the value of ≤0.1 % given in I.S. EN 12620 for use in concrete for aggregates containing pyrrhotite. Overall pyrrhotite equivalent values were determined as between 0.57-1.96 wt%. Fe/S ratio analysis for the analysed pyrrhotite gives a ratio of >0.916 (average of 1.14 from given analysis) confirming iron-enriched monoclinic/hexagonal 6C pyrrhotite. Six samples exhibited increases in visually estimated oxidation of the identified sulphides, most abundantly as conversion of pyrrhotite to iron oxides (goethite & ferrihydrite). Six samples exhibited a notable increase in oxidation, internal fractures and associated spalling. An increase in both internal and peripheral aggregate fracturing was recorded in seven of the nine sulphide-bearing samples. Eight samples exhibited an increase in the proportion of cement paste leaching and alteration from the base-line examinations. Of these, three samples (006, 007 and 010) exhibited major increases in cement paste alteration. Although the thermodynamic conditions of the test samples (fully carbonated, C-S-H heavily altered, high calcium, low PH environment) do not favour the production of sulphates, evidence of sulphate replacement was recorded. More commonly small quantities of gypsum were observed to be incorporated into $CaCO_3$ clusters during recrystallisation and as small crystallites of gypsum formed within or replacing part of the Ca-deficient interstitial Si-Al paste.

Although significant linear expansion was not recorded during the test period, post-test examination confirms that sulphide oxidation and internal sulphate attack has been instigated. As such, by measure of the comparative petrographic examination and condition of the most expansive core in the set (009), the phyllite test set would not meet the conditions to reclassify to a mortgageable class A3 concrete class in line with the RICS guidance. The testing has proven effective at

confirming that under prolonged high moisture conditions pyrrhotite within the phyllite ACMU is susceptible to sulphide oxidation and internal sulphate attack even when the cement paste has carbonated before conditions for oxidation are met. The internal sulphate attack has caused radial fracturing, spalling and alteration of the fully carbonated cement paste, which when associated with the high voidage of the ACMU material appears to have resulted in collapse into voids rather than linear expansion.

References: [1] National Standards Institute of Ireland. IS 465:2018+A1:2020., Assessment, testing and categorisation of damaged buildings incorporating concrete blocks containing certain deleterious materials and Amendment 1:2020. [2] Leemann, Andreas, Barbara Lothenbach, Beat Münch, Thomas Campbell, and Paul Dunlop. "The “mica crisis” in Donegal, Ireland–A case of internal sulfate attack?." *Cement and Concrete Research* 168 (2023): 107149. [3] Royal Institute of Chartered Surveyors. (2015) The Mundic Problem – RICS Guidance note, UK 3rd Edition. London, Royal Institute of Chartered Surveyors

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EVALUATING THE THERMODYNAMIC PROPERTIES OF IRON-CONTAINING SILICEOUS HYDROGARNET

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ABSTRACT

The utilization of iron-rich industrial wastes as raw materials in Portland cement (PC) clinker production has both environmental and economic benefits [1]. However, the usage of iron-rich industrial wastes in clinker leads to a higher iron content, which can affect the hydration product formation. Iron-containing siliceous hydrogarnets are one of the major phases present in hydrated iron-rich PC, but there are very limited studies on their thermodynamic properties. The current thermodynamic data available for iron-containing hydrogarnets in the widely-used database Cemdata18 may not be reliable as the absolute entropy data fitted from the measured solubility product by using three-term temperature extrapolation function [2] differs significantly from the value calculated empirically from a correlation based on the molar volume, which has been proposed for use as a check on such parameter values [3]. The solubility product of the iron-containing siliceous hydrogarnet was measured only at two different temperatures and in the presence of unreacted C_2F, which potentially increases the uncertainty in the data.

This study consists of two parts: In first part, we extended the iron-containing siliceous hydrogarnet thermodynamic database with a larger variety of Al to Fe ratios (0, 0.2, 0.3, 0.5, 0.7, 0.8, and 1.0) [2], the derived data were then used in GEM-Selector software for hydration modeling of PC [4], which was experimentally verified to contain iron-containing siliceous hydrogarnet after hydration. The effect of iron content on the final hydration products was evaluated by varying the C_4AF and C_3A content between 0 to 20 wt.% while keeping their sum constant (Fig. 1a). As the chemical composition of iron-containing siliceous hydrogarnet of the hydration modeling in first part was found to be ($C(A_{1.6}F_{0.4})SH$), we performed a sensitivity analysis of the absolute entropy on its final hydration product formation in PC [4] (Fig 1b). The sensitivity test shows that a small change in absolute entropy (±4%) leads to a significant variation of the final hydration product, showing the importance of accurate, experimentally measured thermodynamic constants of iron-containing siliceous hydrogarnet for a precise Gibbs energy minimization modelling of cement hydration. ,

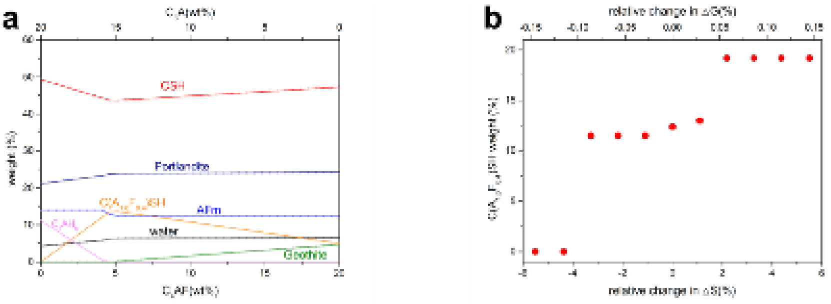

Fig. 1. Influence of Absolute Entropy on the hydration phase assemblage at 25°C. a)

Thermodynamic simulation shows the presence of iron-containing siliceous hydrogarnet ($C(A_{1.6}F_{0.4})SH$), in consistency with the experimental data for $C_4AF/C_3A = 0.62$ [4]. b) Sensitivity study of the absolute entropy of iron-containing siliceous hydrogarnet ($C(A_{1.6}F_{0.4})SH$) on its quantity after hydration for a PC [4] with $C_4AF/C_3A = 0.62$.

References: [1] Peys, A. et al. Cement and Concrete Research, 2022, 157, 106834. [2] Dilnesa, B.Z. et al., Cement and Concrete Research, 2014, 59, pp. 96-111. [3] Ghazizadeh, S. et al., Cement and Concrete Research, 2020,136, 106188. [4] Vespa, M. et al., Journal of the American Ceramic Society, 2015, 98(7), pp. 2286-2294.

Extended Abstracts: Poster Presentations

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UTILIZATION OF NON-METALLIC PRODUCTS (NMPS) FROM RECYCLED ALUMINIUM AS A SUPPLEMENTARY CEMENTITIOUS MATERIAL

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ABSTRACT

Non-Metallic Products (NMPs) are waste materials produced during aluminium recovery comprising high amounts of Al_2O_3, SiO_2, Fe_2O_3, MgO, and CaO. They possess high porosity and specific surface area, making them a promising supplementary cementitious material (SCM) to replace scarce materials such as blast furnace slag. However, their toxic components (AlN, Al_4C_3, AlP, Al_2S_3, and Al_5O_6N), metallic aluminium, and high chloride concentration make their safe use challenging, resulting in their disposal in landfills, and environmental harm.

This study develops new processing technology to make NMPs suitable for use in Portland-based cement and concrete production. Detailed chemical and physical characterisation of industrial NMPs is performed, including X-ray fluorescence, X-ray diffraction, particle size distribution, and Fourier transform infrared spectroscopy, among others. Dissolution behaviour of NMPs in aqueous environments relevant to fresh Portland-based cement blends is also investigated, and pre-treatment methods for eliminating toxic components and chlorides are developed, to make NMP a valuable SCM.

Furthermore, blended Portland cement pastes were produced using a variety of NMPs, and their phase assemblage and microstructure is assessed. This provides new insight into viability of NMPs as an SCM, and is critical in finding ways to upcycle these materials effectively while minimizing their impact on the environment.

REGULATION, RISK AND CONVEYANCING IN IRISH DEFECTIVE CONCRETE

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ABSTRACT

Since the early 2000s, defective concrete blockwork used in Ireland has contributed to the degradation of several thousand homes, many of which require complete demolition. The primary causes relate to the geological properties of the aggregate used. In Donegal, the problems are associated with certain Dalradian metasediments, which produce abundant free mica in the cement binder and contain pyrrhotite concentrations that exceed aggregate compliance values. In other counties, the problems are mostly related to the presence of framboidal pyrite within calcareous mudstones and argillaceous limestones quarried from the Carboniferous lithologies. Along with some outstanding questions over failure mechanisms, there are practical concerns over when defective blockwork was used, the regulation constraining the aggregate that can be used, and long-term implications for property transactions.

With respect to properties built using defective concrete block, there is evidence of a primary risk window from the late 1990s up until the 2008 credit crunch. Outside of this there is emerging evidence of the use of problematic aggregate after the credit crunch and before the late 1990s throughout Ireland, though to a far lesser extent. The two main problematic aggregates (phyllite in Co. Donegal, and black limestone in other Counties) have very similar risk windows, but the question of the total number of affected properties remains currently unknown. Estimations currently run to between 5,000 and 7,500 properties, spread across up to 12 counties.

With respect to sulphur compliance values, EN12620 guidance constrains the pyrrhotite concentration of aggregate to be <0.1% total sulphur (TS) and came into force in Ireland in 2002. Phyllite aggregate exceeds this compliance value and its use within Co. Donegal runs for at least a decade past 2002. The EN12620 codes for aggregate containing pyrite allow for up to 1.0% TS and means that much of the defective concrete block observed through the other counties of Ireland are technically compliant. Nonetheless, the presence of framboidal pyrite within problematic aggregate has been implicated in numerous cases of property degradation. This was previously recognised with the mundic guidance for SW England which restricted total sulphide content to 1.0% [1] where similar problematic aggregate is present, equivalent to ~0.6% TS assuming a typical acid soluble sulphate content of 0.2%. Furthermore, the compendium of aggregates used in SW England postulated that a sulphide content of just 0.2% may be sufficient to cause major damage [2] and I.S.465 guidance recognises the risk inherent to framboidal pyrite hosted in weak aggregate [3]. Taken together there is strong evidence that the EN12620 guidance value for pyrite within aggregate needs to be much lower when the more reactive framboidal pyrite is present and the hosting aggregate is weak.

At present damaged properties are being tested for application to the defective concrete block (DCB) scheme on the basis of degradation recorded by a building conditions assessment (BCA) report. However, with respect to conveyancing, the DCB and I.S.465 standard are designed to determine the extent of damage and the nature of the aggregate in use. There is now a necessity to formalise a long-term testing regime for properties not currently displaying damage that are to be bought and sold within the conveyancing market. The testing regime used for the conveyancing market needs to provide certainty to buyers and lenders that their purchase is safe and give homeowners more clarity on how they can sell or remediate their property, particularly for those gaining Low/Medium Risk classifications as part of an I.S.465 assessment protocol.

References: [1] Royal Institute of Chartered Surveyors. (2015) The Mundic Problem – RICS Guidance note, UK 3rd Edition. London, Royal Institute of Chartered Surveyors. [2] Bromley, A. (2002) A compendium of mundic aggregate used in SW England. [3] National Standards Institute of Ireland. IS 465:2018+A1:2020., Assessment, testing and categorisation of damaged buildings incorporating concrete blocks containing certain deleterious materials and Amendment 1:2020.

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THE INFLUENCE OF RECYCLED AGGREGATE AND NATURAL POZZOLANA ON THE COMPRESSIVE STRENGTH OF CONCRETE

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ABSTRACT

Using recycled aggregate coming from construction wastes is widely known as an effective way to conserve natural resources, provide a renewable source of construction materials and solve the increasing waste disposal crisis .

This experimental study investigated the effect of using different proportions of Recycled Coarse Aggregate (RAC) on both the bulk density and the compressive strength of the concrete that comprises it. This study also discussed the influence of incorporating the Natural Pozzolana on improving the long term compressive strength when added to the concrete as a replacement or as an additive to cement.

To prepare the samples for this study, the RAC was obtained from crushing the waste concrete of laboratory test cubes. The RCA particles' size ranged between 25mm and 4.75mm. No fine recycled aggregate was used in this research. The Natural Pozzolana was imported from As Suwayda in south Syria, and it was used after it was grounded to the same fineness as the Portland cement.

The concrete mixes were produced with water to cement ratio of 0.55 and target compressive strength of 30MPa. The testing program involved three concrete sets. The first set included four concrete mixes that were prepared using four percentages (0%, 50%, 75%, 100%) of the RCA as a replacement of the Natural Coarse Aggregate (NCA). The second set was the same as the first set, but the Natural Pozzolana was used (by 15% of cement weight) as replacement of the cement, whereas for the last set, the Natural Pozzolana was used (by 15% of cement weight) as an additive to the concrete mixes. In total, there were 12 different concrete mixes to evaluate the impact of RCA and Natural Pozzolana on some of the physical and mechanical concrete properties.

In this research, some RCA characteristics were measured and compared to that of NCA. The comparison revealed that the RCA had 2 times higher absorption and around 5% lower density than NCA, and this is due to the large amount of old mortar attached to the recycled aggregate.

In this paper, the dry bulk density was identified for all the mixes. The data showed that the bulk density of concrete slightly decreases with increasing the content of the recycled aggregate.

Additionally, the compressive strengths at age of 7, 28, 56 and 120 days of all mixes were reported, and on the basis of the comparative analysis of the experimental results, the following conclusions could be drawn: (1) the compressive strength decreases as the proportion of the RCA recycled aggregate increases; (2) it was possible with help of Natural Pozzolana as an additive to produce a concrete, made only from RCA, which satisfies the target compressive strength 30Mpa at age 120 days; (3) the results exhibited that the best combination of RCA and NCA was when 50% of each were employed along with Natural Pozzolana as an additive by 15% of cement weight, the achieved compressive strengths were almost equal to that of concrete mix with only NCA at all ages; (4) the lowest compressive strength achieved at early age (28 days) was when utilizing 100% of RCA with Natural Pozzolana as an additive, the drop was up to 25% compared with the mix

prepared with only NCA; (5) No considerable change was reported in compressive strengths when Natural Pozzolana was used as a partial substitute for cement if the same blend of aggregate was applied. This fact could contribute to reducing concrete cost, as this mineral admixture is cheap and available.

All in all, the observations of this research confirmed that the use of recycled coarse aggregate along with the cementitious materials, such as Natural Pozzolana, is likely to present similar behaviour of one made using natural coarse aggregate, so it is likely to be a viable option for structural use.

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THE EFFECT OF SLAG CHEMISTRY ON THE PORE STRUCTURE OF NA2SO4-ACTIVATED SLAG CEMENTS UNDER ACCELERATED CARBONATION

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ABSTRACT

1. Introduction

In this study, three blast furnace slags with varying Mg/Al ratios were activated with a sodium sulfate solution to produce cement pastes. The degree of slag reaction (DoR), change of pore structure and transport properties were studied in Na_2SO_4-activated slag cement, before and after accelerated carbonation exposure.

2. Materials and Methods

A non-destructive synchrotron-based X-ray computed tomography (XCT) was used to characterise the pore network of cement pastes. The complementary DoR was determined by image analysis of backscatter electron images using scanning electron microscope (SEM). Trainable machine learning WeKa algorithm was used to conduct phase segmentation. Thermodynamic modelling software GEMs was used to predict the phase assemblage of Na_2SO_4-activated slag cements.

3. Main results

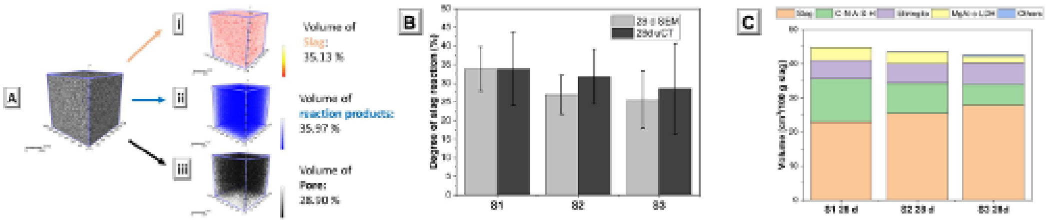
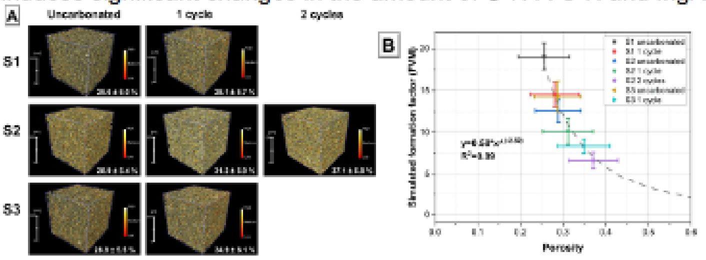


Fig. 1. (A) example of 3D rendering of reconstructed tomography of Na_2SO_4-activated slag cements showing (i) segmented slag; (ii) reaction products; (iii) pore**. Fig. 1. (B)** Comparison of DoR determined by SEM and uCT. **Fig 1. (C)** Predicted phase assemblage using GEMs.

The DoR of slag is strongly dependent on the intrinsic properties of slag used (e.g. chemical composition). Comparable quantities of ettringite are predicted to form when using the three slags studied. The slag type induces significant changes in the amount of C-N-A-S-H and MgAl-LDHs in Na_2SO_4-activated slag cements.



Accelerated carbonation leads to increased porosity and decreased formation factor. The simulated formation factor based on the pore structure of uCT images agrees with Archie's law. Cement pastes using slag with higher Mg content form denser microstructure and features higher carbonation resistance.

Fig. 2. (A): 3D rendering pore structure of Na_2SO_4-activated slag with their porosity values using 3 slags, before and after accelerated carbonation. **Fig. 2. (B):** Segmented porosity vs simulated formation factor.

3. Conclusion

Na_2SO_4-activated slag cements can reach DoR of ~30 % after 28 days of curing. The trainable WeKa algorithm was successfully applied to quantify DoR and porosity in cementitious materials with the estimation of statistical errors. Application of the finite volume method in uCT image enables simulation of the formation factor, agreeing with Archie's law. Slag with rich Mg content shows higher DoR and produced cements with higher carbonation resistance. Accelerated carbonation leads to a more porous microstructure with a decreased formation factor. This study demonstrates how XCT can improve our understanding and prediction of novel cementitious materials' durability.

CHARACTERIZATION OF PORE STRUCTURE EVOLUTION IN ALKALI ACTIVATED SLAG CEMENTS USING TIME-LAPSED IN-SITU X-RAY COMPUTED TOMOGRAPHY AND SCANNING ELECTRON MICROSCOPY

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ABSTRACT

1. Introduction:

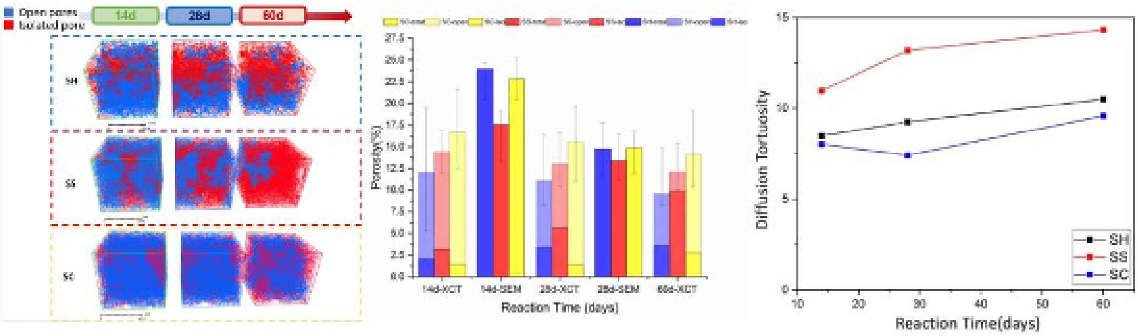
Alkali-activated slag cement (AASCs) is gaining prominence for its eco-friendly credentials compared to traditional Portland cement. This study assessed the pore structure evolution of AASCs as a function of the activator chemistry using microscopy techniques, at different magnifications.

2. Materials and Methods:

AASCs were synthesized using blast furnace slag and NaOH, Na_2SiO_3, or Na_2CO_3 as alkaline activators. A non-destructive 3D pore network analysis was conducted employing X-ray CT (XCT) imaging, at different curing times. Complementary porosity was determined by image analysis of results collected using scanning electron microscopy (SEM).

3. Main Results:

XCT and SEM results revealed that (1) the sodium silicate system develops the lowest overall porosity, accompanied by rapid reductions in open pores and a pronounced increase in tortuosity over the curing time. This observation suggests a less interconnected micro-scale pore structure. (2) the sodium hydroxide system developed comparable total porosity to the sodium carbonate system, however, the porosity within the sodium hydroxide system predominantly consists of 100nm-1um pores.



(a) (b) (c)

Figure 1 (a) The 3D pore network evolutions of three activators activated AASCs by XCT, SH: sodium hydroxide, SS: sodium silicate, SC: sodium carbonate. **(b)** Pore structure evolution of AASCs as a function of the activator type and curing ages, determined by XCT and SEM. **(c)** Diffusion tortuosity of pore structures in the three AASCs over time, determined through XCT imaging-based simulation (Random Walkers).

4. Discussion and Implications:

In general, comparable porosities were identified, in a given cement evaluate via image analysis of XCT or BSE results. A low porosity and less interconnection of the pore structure in sodium silicate system suggests that the microstructure is denser and more homogenous, compared with SH or SC activated cements. These characteristics potentially contribute to optimizing transport properties of AACs, which might result in an improved durability.

5. Conclusion:

Activator chemistry significantly influences the pore structure development of alkali-activated slag cements. Comparable pore structures were identified in sodium hydroxide/sodium carbonate activated slag cements. Sodium silicate-based cements present a slightly lower porosity to other systems but a much higher diffusion tortuosity.

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MAGNESIUM PHOSPHATE CEMENT AS AN ALTERNATIVE ENCAPSULANT TO TREAT HIGHER ACTIVITY RADIOACTIVE WASTE

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ABSTRACT

The Encapsulants Integrated Research Team (EIRT) is a collaborative programme between Sellafield Ltd (SL) and the National Nuclear Laboratory (NNL) to evaluate potential encapsulants for the treatment of Higher Activity Waste (HAW). As a result, work has been carried out investigating magnesium phosphate cement (MPC) systems. MPC has potential advantages for the treatment of HAW compared to traditional Portland cement (PC) based grouts. This includes high fluidities and low viscosities, low content of free water, and near-neutral pore solution pH to potentially reduce amphoteric metal corrosion.

A factorial test matrix design was used to give a total of 40 x 3 L mixes covering a range of formulation combinations. The parameters studied were:

- MgO:KH2PO4 molar ratio (M:P) – 1.75:1 to 2.5:1
- Geoflash S® metakaolin filler mass ratio (F) – 0.25 to 0.40
- Boric acid (B) retarder to MgO (M) mass ratio (B:M) – 0.18 to 0.27
- Dead burnt magnesium oxide DBM 90 grade (60 mesh):DBM 90 grade (200 mesh) mass ratio – 0:100, 50:50, 100:0
- Water/cement ratio (w/c) – 0.44 to 0.50
- Shear – low (62 rpm) and high (4500 rpm)

Each mix was assessed for processing properties (set, bleed, heat of hydration (HoH), viscosity, fluidity) and product quality (compressive strength, ultrasonic pulse velocity (UPV), dimensional stability) up to 90 d.

Processing property results indicate all mixes produced grouts that had higher fluidity and lower viscosity than PC-based grouts typically used for HAW treatment and were well within guidelines for PC based grouts when considering bleed and HoH. Bleed was only observed in four formulations and was ≤2% of the total volume in all cases. HoH traces typically showed a cumulative heat output below the historical guideline of 180 kJ/kg for PC-based encapsulation grouts. Set times were more variable with all formulations achieving initial set in ≥3 h, but some mixes with lower filler content exhibiting set times >48 h. Notably, all mixes at the highest filler loading (0.40) reached final set ≤48 h regardless of other formulation variations, suggesting a higher filler ratio in the mix contributes to shorter set times.

All but one MPC mix studied produced products with strengths exceeding guidelines for historic cemented HAW products, with statistical analysis indicating higher filler loadings, low water content and increased curing time are conducive to increased strengths. Strengths typically increased up to 28 d, after which they plateaued to 90 d. This was also seen in the UPV data, where minimal changes were visible between 28 d and 90 d. Dimensional stability measured up to 90 d indicated a modest decrease in microstrain (shrinkage) across most formulations, with all formulations well within historical guidelines.

Preliminary powder X-Ray Diffraction (pXRD) and Scanning Electron Microscopy (SEM) have been carried out on four formulations which indicate that the main phase present is K-struvite, an

insoluble crystalline hydration product capable of binding free water. The majority of the K-struvite has formed by 7 d with minor increases up to 90 d.

Overall, MPC grouts warrant further investigation within a more refined formulation range. Statistical analysis indicated that shear and DBM particle size do not significantly affect resultant product properties, while the boric acid range was too small to show the effect of this retarder on the system.

Acknowledgements: The authors would like to express their gratitude to Sellafield Ltd for funding this project.

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EXPLORING FEASIBLE METHODS FOR UTILIZING RHA AS COMPONENT IN CEMENT BINDERS

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ABSTRACT

The combustion of rice husk produces a by-product called rice husk ash (RHA). The chemical composition and its accessibility make it a possible part replacement for Portland cement in concrete. However, the properties of RHA vary due to the different conditions such as the source of rice husk and process conditions (combustion temperature and duration). RHA produced through uncontrolled burning can potentially lead to water demand-related problems which in turn results in poor pozzolanic activity [1]. Under such circumstances, utilizing RHA as a cement substitute in concrete is not beneficial [2]. RHA can be further treated by calcination and grinding to enhance its properties [3]. In spite of the existing literature on the effects of the burning and grinding processes on the properties of RHA, it is not evident the effect of the priority order between these two processes on the quality of RHA. The primary objective of this study is to propose RHA treatment guidelines and present a potential pathway for achieving favourable properties in RHA-blended cements. For this purpose, supplied RHA were processed as follow: 1) Grinding before Calcination (GCRHA); 2) Calcination before Grinding (CGRHA). Preliminary results showed that the proposed treatment had a minor effect on the silica characteristics of as revealed by XRD. In contrast, there is an impact on loss on ignition (LOS) values and the pozzolanic activity of RHA between calcination and the grinding process. Grinding RHA before calcination it seems unsuitable due to concerns about breaking down the cellular structure, resulting in increased particle packing and agglomeration, causing the heating process to be uneven and difficulty in thorough burning. On the other hand, calcination of RHA before grinding was found to be a more effective approach, as it is believed that the cellular structure of rice husk ash absorbs more heat uniformly during calcination within the pores, leading to a more efficient burning process and higher pozzolanic activity. This work provides the basis for further recommendation to enhance chemical and physical properties of RHA as cement replacement.

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PERFORMANCE AND DURABILITY OF LOW-CARBON CONCRETE CONTAINING WASTE PLASTICS AND EXPOSED TO MARINE ENVIRONMENT

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ABSTRACT

The demand for concrete production driven by rapid urban development significantly contributes to global CO_2 emissions. One proposed solution is to replace natural aggregates with alternative materials such as recycled plastics. However, to meet existing standards and regulations, long-term performance must be demonstrated to ensure structural integrity and resilience. Concrete deterioration is often observed in coastal and tidal infrastructures, which endure extreme temperature and moisture fluctuations, wet/dry cycles, and exposure to saline water. Only limited knowledge exists regarding the performance of concrete made using natural aggregate replacements. As the world moves towards a net-zero future and renewable energy technologies gain momentum, tidal range scheme projects are being constructed in harsh environments. Given the substantial amount of concrete required for these projects, it is imperative to ensure their sustainability and minimise their environmental impact. The objective of this study is to assess the impact of marine exposure conditions on low-carbon concrete specimens. These specimens were produced using supplementary cementitious materials, SCMs (silica fume, fly ash, and rice husk ash) and commercial recycled plastics including polystyrene and acrylonitrile butadiene styrene (Axplas® MEP54) as partial coarse aggregate. Specifically, the study focused on the early age and longer-term properties of low carbon concrete exposed to marine environment. The aim is to understand how aggressive environmental conditions, such as sea water and intertidal action wet/dry (high/low tide) cycling, influence the mechanical performance and durability of the concrete. Key properties examined included compressive strength, flexural strength, water absorption, concrete bulk resistivity, porosity, shrinkage potential and moisture content. To achieve these objectives, concrete cube, cylinder, and prim specimens were prepared with four mix designs; control (conventional concrete), low carbon (made with 40% cement replacement), low carbon with 10% plastic aggregates, and low carbon with 30% plastic aggregates. Each batch of specimens was duplicated, with one batch deployed on-site (Pembroke Docks, UK), while the other batch was kept under laboratory conditions for comparison. Preliminary results showed that the 28-day compressive strength of the control series was the highest followed by low carbon, low carbon 10% plastic, and then low carbon 30%, respectively. The drop in compressive strength reached 50% decrease in samples with 30% plastic. Site specimens subjected to intertidal conditions, showed a decrease in strength compared to those cured at laboratory conditions, due to the inclusion of salt precipitate within the pore structure. Specimens exposed to site conditions exhibited a slightly lower flexural strength compared to lab cured specimens. A decrease in porosity on specimens collected from site was observed. This decrease can be attributed to the presence of salt crystalline phases in the internal voids [1]. As such, thermal conductivity values were in the range of 1.1–1.8 W/m °C, with lower values recorded for samples containing plastics. The increase in plastics replacement resulted in a decrease in thermal conductivity by around 39% compared to the control specimens. This is due to the inclusion of recycled plastics with a much lower density as opposed to the concrete constituents. Bulk electrical resistivity measurements indicated that with the presence of SCMs led to a higher resistivity (approximately 45 kΩ cm), resulting in a subsequent reduction in chloride penetration potential in comparison to the control series (6 kΩ cm) [2], [3]. This reduction further increased with increasing the plastics content, highlighting positive impact of incorporating SCMs and plastics on concrete's resistance to chloride ingress. Preliminary results have shown that recycled plastics can be used as a replacement material for natural aggregate up to 10–30%, coupled with up to 40% Portland cement replacement materials. The strength gained

after 28 days of both laboratory conditions and sea water exposure reached acceptable “structural” values. Low carbon concrete provided a higher resistance to chloride penetration both at laboratory and site conditions.

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PERFORMANCE OF CONCRETES PREPARED WITH BLENDED CEMENT CONTAINING CALCINED EXCAVATED LONDON CLAYS

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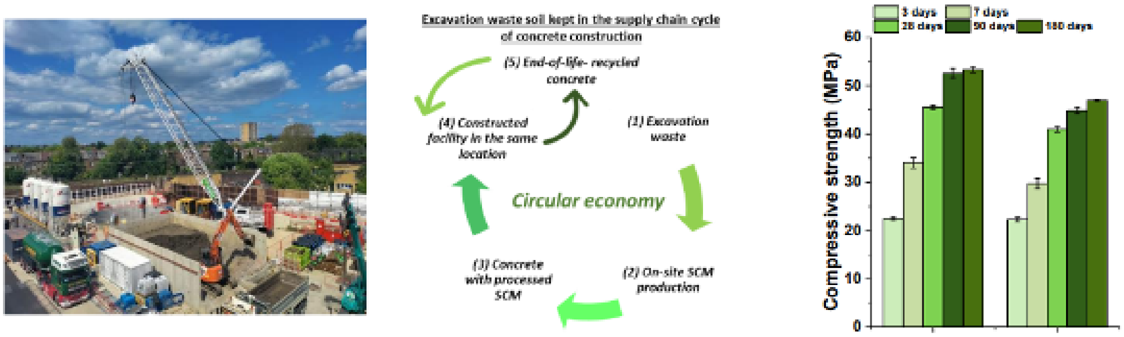
ABSTRACT

By replacing a large portion of Portland cement with calcined clay, carbon emissions associated with concrete production can be significantly reduced, enabling achieving net-zero targets in construction projects. Vast amounts of soil waste (Fig 1a) generated from major infrastructure projects could serve as a valuable resource for producing cement replacements or supplementary cementitious materials (SCMs); however, it is largely unknown whether the use of low-purity low-kaolinite-containing clays (labelled as CC20 due to 20% kaolinite content in the raw clay before calcination) will produce resilient concretes. This study investigated the feasibility of using low-purity calcined clay, derived from excavation waste from the Greater London area, as an SCM in the production of concrete (Fig 1b). Specifically, it explored the effect on concrete's performance of replacing CEM I with calcined excavated London clay (30 wt.% replacement, denoted in Fig 1c as CC20) , or by replacing CEM I with 30 wt.% calcined clay plus 15 wt.% limestone, denoted here as CCL20. Concrete mixtures were prepared with a binder content of 360 kg/m^3 and a water-to-binder ratio of 0.5, as per BS 8500-1 recommendation for 50-year service life with chloride exposure (CEM IIB and IIIA requirements in XS3). Mechanical properties were monitored for a curing period of up to 180 days. Additionally, durability performance of such concretes was evaluated in terms of chloride permeability and accelerated carbonation test. The results revealed concrete containing excavated London clay achieved a compressive strength of about 40 MPa by 28 days of curing in both binary and ternary cement systems (Fig 1c). These calcined clay concrete also exhibited increased chloride resistance (chloride migration coefficient of < 3.5 x 10^{-12} m^2/s in both binary (CC20) and ternary (CCL20) concretes) compared with CEM I concretes (chloride migration coefficient of 7.16 x10^{-12} m^2/s). This outcome demonstrates the high potential of utilizing low-purity calcined clay (< 30% kaolinite content) obtained from excavation activities to produce sustainable and durable concretes.



(a) Excavated London Clay (b) Circular use of Excavation waste (c) Compressive strength

Figure 1 Circular use of excavation waste as SCM resource to produce sustainable concretes.
Note: CC20 is binary mix containing 30% of calcined excavation waste and CCL20 stands for calcined clay-limestone combination containing 30% calcined clay and 15% limestone replacement.

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UNDERSTANDING THE RELATIONSHIP BETWEEN REACTION MECHANISMS AND KINETICS OF ALKALI ACTIVATED SLAG CEMENT AND FRESH STATE PROPERTIES

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ABSTRACT

Alkali activated cements (AACs) are often noted for their potential to reduce cement-associated CO_2 emissions by up to 80 % through their incorporation of industrial waste and/or by-products as well as naturally occurring minerals. Despite this, the commonly used activators – alkali silicates and hydroxides – carry greater embodied carbon emissions than their less widely used counterparts, alkali carbonates, which are typically naturally occurring or can be produced from CO_2 sequestration. The limited use of these alkali carbonates at present in the production of AACs is attributed to their lengthy initial setting and hardening time, as well as their poor early strength development.

This study aims to explore the relationship between reaction mechanisms and kinetics in carbonate-activated slag binders and their physical property development in comparison with silicate-activated cements, using various spectroscopic and microstructural characterisation techniques, including isothermal calorimetry, zeta potential measurements, in-situ FTIR, and NMR. In conjunction with investigating the flow characteristics of AACs in the fresh state, this study optimises formulations of alkali activated slag binders for enhanced workability, mechanical properties, and durability. This understanding is fundamental for driving implementation of AACs in industry and thus minimising the environmental impact from CO_2 emissions associated with the cement and concrete industry.

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INFLUENCE OF GAMMA-IRRADIATION ON THE PROPERTIES OF MAGNESIUM-SILICATE-HYDRATE CEMENT MORTARS

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ABSTRACT

UK MAGNOX nuclear reactors produced a magnesium-based alloy cladding waste, which contains traces of uranium and other radioactive components. Incorporating the waste as a raw material into an encapsulation matrix, such as a magnesium-silicate-hydrate (M-S-H) mortar, could reduce the final volume of containers requiring long-term storage.

Determining the influence of gamma-irradiation on the properties of an M-S-H mortar is key to understanding the viability of M-S-H as an immobilisation mortar. A magnesium hydroxide ($Mg(OH)_2$) based M-S-H mortar, with samples aged to 28 days, 6 months or 1 year, was irradiated to 1 MGy or 5 MGy. Properties, including compressive strength and porosity, were tested, and characterisation techniques, such as x-ray diffractometry were used to characterise the microstructural changes. Changes in properties were observed for all mortars, with greatest changes observed at 5 MGy. At early ages, radiogenic heating had the greatest influence, increasing strength through M-S-H formation, but also porosity due to dehydration. At 1 year, a reduction in porosity and strength is observed, most likely due to M-S-H bond rearrangement.

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INFLUENCE OF STEAM CURING PARAMETERS ON CONCRETE STRENGTH AND OPTIMIZATION AT 28 DAYS

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ABSTRACT

Steam curing provides moisture and increases the temperature, which is important, factors for accelerating the concrete curing process. This paper is the second the author series that identifies the effect of atmospheric -pressure steam curing parameters for producing precast concrete. These parameters include a delay period after casting (DT) of 0, 2, 3, and 4 & 6 hours, maximum curing temperatures (T) of 50, 60 &70oC maintained for a specific curing period (CT) of 2, 3, 4 and 5 hrs. To attain this aim, several laboratory experiments have been carried out to measure and optimize compressive strength after 28 days. Taguchi methodology has been utilized to identify that DT,CTand T have the same weight effective on compressive strength and DT=3hrs, CT= 4hrs and T= 70oC as the optimum curing regime at 28 days (store on air) after steam curing .the optimum steam curing cycle will be carried out that to compare with the values of compressive strength specimens subjected to conventional water curing method at different ages which results showed that the optimum steam cured type has better performance than water curing at early age.

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EFFECT OF GRAPHENE OXIDES DERIVED FROM THE WYOMING POWDER RIVER BASIN COAL ON THE COMPRESSIVE STRENGTH OF CONCRETE

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ABSTRACT

Cementitious materials, including concrete, are widely used in construction. Various methods have been employed to enhance the mechanical properties of concrete. This study focuses on exploring the potential of various graphene oxide (GO) types derived from Wyoming Powder River Basin (PRB) Coal on improving the compressive strength of concrete. Various PRB coal-based GO types were developed including GO and nGO from coal char pyrolyzed at 850 and 1100 ºC, respectively, with both treated with nitric acid, and rGO with additional heat treatment at both 200 and 1100 ºC. A systematic study of the effect of these GO types on the compressive strength of concrete was conducted. The findings reveal that the GO provides a higher concrete compressive strength than the other GO types. The substitution of cement with GO led to an initial gain in compressive strength. However, further increasing the GO content decreases the compressive strength. Particularly, the optimal combination of a water/cement ratio of 0.60 and a GO content of 0.05 wt.% results in a remarkable 20.5% increase in 28-day compressive strength. This study highlights the promising potential of utilizing GO derived from PRB coal as an effective additive in concrete to enhance its compressive strength.

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SYNTHESIS OF SODIUM IRON SILICATE HYDRATE (N-F-S-H)

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ABSTRACT

Alumina production generates vast quantities of bauxite residue that can be processed into Fe-rich cementitious materials such as a precursor for alkali-activated materials (AAM). Typically AAM utilises Ca-poor precursors, culminating in a binder comprising a nanocrystalline zeolite-like alkali aluminosilicate (hydrate) phase, often referred to as N-A-S-(H) gel. However, the chemistry of alkali-activated materials derived from Fe-rich precursors, such as bauxite residue, remains largely unexplored, especially whether Fe can play an analogous role to Al in the binding phase.

This study reports the characterisation results of samples with a Fe/Si mol ratio of 0.5 and synthesised at 50 °C using $FeCl_3 \cdot 6H_2O$ and fumed silica, targeting the precipitation of sodium iron silicate hydrate (N-F-S-H) over time. NaOH is added to maintain a high pH to increase Fe solubility. TGA, FTIR, and XRD reveal that initially, N-F-S-H is formed.

The XRD results show that goethite is not present in the samples with a Fe/Si mol ratio of 0.5. This indicates that no crystalline FeO(OH) is present in the N-F-S-H samples. However, since some of the solids synthesised had a brownish colour, we expect that some of the samples contain traces of poorly crystalline iron hydroxide phases. Halite could be observed in the system, even if the solids were washed with ethanol to eliminate dissolved ions.

In the FT-IR spectra for N-F-S-H samples, the broad signal centred at 3357 cm^{-1} is caused by sorbed H_2O molecules on the solids, usually poorly or nanocrystalline solids as C-S-H or N-A-S-H. The small band observed at around 1653 cm^{-1} for each sample that is assigned to O-H of the bending H_2O molecules. The peaks at 1375 cm^{-1} correspond to the Fe-OH band, indicating the appearance of the poorly crystalline iron hydroxide phases. The Si-O stretching band of the N-F-S-H samples is centred at 936 cm^{-1}, which is usually characteristic of Q^2 or Q^3 silicate coordination. This effect can be related to Fe^{3+} binding as a network former in the silicate network. Three characteristic peaks for goethite, located between 700 cm^{-1} and 900 cm^{-1}, and another at 620 cm^{-1}, are not present in the FT-IR spectrum of the N-F-S-H samples, confirming that no goethite is present in the samples.

The TGA results show that the N-F-S-H samples contain gel water (as indicated in the FT-IR spectra), which is identified by the peaks at 120 °C, suggesting that N-F-S-H might be present in these samples after 7 days of equilibration. Comparing the N-F-S-H samples to TGA data for goethite, which has a well-defined weight loss in the temperature range centred at 265 °C, the results confirmed again that goethite is not present in the N-F-S-H samples. These TGA results are consistent with the FT-IR analysis, which confirm the presence of N-F-S-H in the samples through the presence of Q^2/Q^3 silicate coordination.

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TOWARDS CONCRETE DECARBONISATION – A PRACTICAL INSIGHT INTO FLY ASH AND BLAST FURNACE SLAG-CONTAINING CONCRETES

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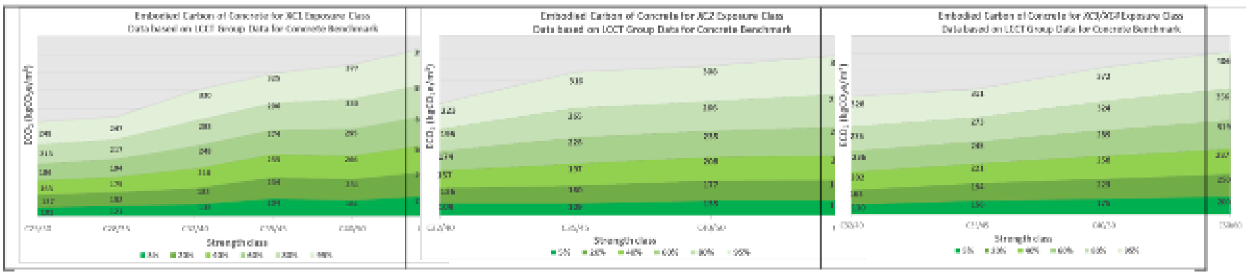
ABSTRACT

Introduction: The significance of decarbonising concrete cannot be understated, as the use of concrete accounts for approximately one-third of the UK construction industry emissions. Concretes produced with lower carbon emitting alternatives to Portland cement, like those blended with pulverised fly ash (PFA) and ground granulated blast furnace slag (GGBS), have been commonly used in the UK. However, there is a growing concern about their long-term availability, and how best those concrete can be used for targeted applications where their unique performance is essentially required. The present study thus focused on evaluating the embodied carbon (ECO_2) of these concretes considering their specific application in terms of in-service exposure conditions.

Methodology: A database of industry-produced concrete mixes was created, selecting mixes designed to comply with corrosion induced by carbonation exposure classes (XC). Mixes were selected based on structural element type and mix design constituents in accordance with BS 8500-1:2015+A12016, targeting a 50-year service life. The ECO_2 was obtained by multiplying the material quantities of the concrete constituents by their cradle-to-gate ECO_2 factors. The ECO_2 factors for the pulverised PFA/GGBS and cement were obtained from the Mineral Product Association factsheet and Environmental Product Declarations, while the ECO_2 carbon factors for the remaining concrete constituent materials were adapted from ICE database (ICE 3.0). The data source for the ECO_2 carbon factors indicate that there has been no allocation of impact from the respective primary processes of iron manufacture and coal fired power stations for both GGBS and PFA.

Results and Discussion: The results below show that the ECO_2 range for XC1 and XC3/XC4 industry produced concretes were higher than those of concretes designed for the XC2 class. The variations in all classes were statistically significant at 0.05 significance level. Based on the variations in ECO_2, the mixes for each exposure class were further categorised into optimised and unoptimised regions considering the total blended cement binder content and the PFA/GGBS amount in the binder, and concrete strength class. The preliminary results indicate that up to 40% PFA/GGBS is required to achieve an optimised reduction in ECO_2, for the XC exposure class, for a broad range of compressive strengths.



Conclusion and Recommendation: The ECO_2 of concrete containing PFA and GGBS depends partly on the environment for which the concrete is proposed to be used. The realisation of a significant abatement in ECO_2 levels within concrete necessitates the substantial utilisation of PFA and GGBS, thus demanding their considerable consumption. Hence, the outcome of this study consolidates the growing concern about the availability of PFA and GGBS to consistently decarbonise concrete up to the year 2050, in accordance with the overarching goal of achieving a

state of carbon neutrality. It is therefore recommended that further research of current concrete mix design practices is conducted, as well as the evaluation of PFA and GGBS containing concretes as viable and meaningful long-term solution for concrete decarbonisation.

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IMPACT OF CARBONATION ON CHLORIDE PERMEABILITY OF COMPOSITE PORTLAND CEMENT-SLAG-LIMESTONE CONCRETES

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ABSTRACT

It is known that low clinker cements are prone to higher carbonation than pure Portland cement (PC) (1), however, the effect of carbonation on the microstructure of ternary cement concretes and its implications on subsequent performance remain unclear (2, 3). This understanding is critical as ternary cements such as CEM VI are being more widely used. Carbonation alters the phase assemblages and porosity, and consequently will affect chloride ingress and the chlorides binding capacity of ternary cement concretes. In this research, the chloride permeability of carbonated concretes made of CEM I, blended with blast furnace slag (binary) and with blast furnace slag and limestone (ternary) were studied in samples exposed to accelerated (3% CO2) or natural carbonation exposure.

Four concretes were studied including plain PC (N), binary slag (NS; ~50% slag), ternary slag-limestone (NSL; ~40% slag and ~10% limestone, and NS2L; ~30% slag and ~20% limestone). Concretes were mixed at a 0.5 water-to-binder ratio, and sulphate level maintained at 3%. 100ϕ x 200 cylinders were cast, demoulded and moist room cured for 28 days. Sawn (100ϕ x 50) mm cylindrical specimens were subjected to unidirectional accelerated (3% CO2; 60% RH) or natural carbonation according to EN12390-12, as shown in Figure 1.

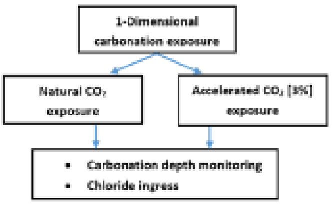

Figure 1: Experimental flow chart

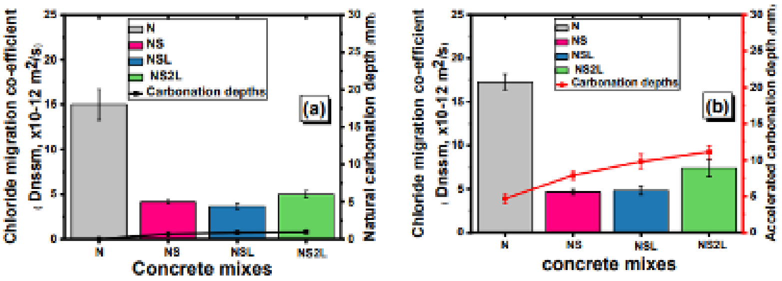

Figure 2: chloride migration post carbonation (a): 28 days natural (b): 28 days accelerated
Dnssm error bars correspond to 28 readings. Carbonation depth error corresponds to 10 readings

After 28 days of CO2 exposure, the carbonation depths were recorded, and concretes chlorides permeability was subsequently assessed according to NT Build 492. Results show (Figure 2) that the slag blended cement with or without limestone (NS, NSL, NS2L) had lower carbonation resistance than the reference CEM I (N) concrete. After 28 days of accelerated carbonation exposure, higher carbonation depths do not result in a significant reduction in chloride permeability of composite concretes i.e., performance reduced close to N. The accelerated carbonation depth in ternary concretes (with 20% limestone addition) is ~10-folds greater than in corresponding natural exposure, but its chloride permeability is not drastically impaired post-accelerated carbonation. This can be attributed to initial pore refinement that retains the pore-blocking effect upon carbonation exposure. However, long-term carbonation exposure needs to be evaluated to confirm if further changes induced by carbonation can affect chlorides permeability of binary and ternary slag blended concretes.

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42nd Cement and Concrete Science Conference
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THE USE OF THERMODYNAMIC MODELLING FOR THE CHARACTERISATION OF ENCAPSULATION CEMENT AND BACKFILL

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ABSTRACT

The UK nuclear industry uses cementitious binders to encapsulate Intermediate Level Waste (ILW). These waste packages will ultimately be placed in a Geological Disposal Facility (GDF), where Nirex Vault Reference Backfill (NRVB) grout will seal the packages in the facility.

NRVB is an Ordinary Portland Cement (OPC)/limestone/$Ca(OH)_2$ blend, specifically created as a reference grout for GDFs to provide a dissolution buffer, so that hydrate phases from the backfill will undergo preferential dissolution when in contact with groundwater. Understanding long-term leaching/ conditioning at an interface between encapsulation cements and NRVB over long time scales will strengthen the GDF safety case.

NRVB and two encapsulation grouts have been exposed to a number of temperature scenarios over the last 13 years; ambient, 35°C and 80°C, reflecting the envisioned short and long-term GDF temperatures after backfilling. Using both old and new experimental data, a model is being developed using thermodynamic software. Its aim is to predict how these cements (at the interface between the 2 and individually) will evolve over the coming centuries, to provide additional data to support both the safety case for the GDF and the use of these cements for the encapsulation of radioactive waste.

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PANORAMIX VERSION 1.0: AN ALGORITHM FOR DESIGNING LOW CARBON CEMENT WITH HIGH DURABILITY PERFORMANCE

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ABSTRACT

Decarbonising concrete through clinker substitution could worsen its durability due to necessary changes in its chemistry. This raises an urgent need to balance CO_2 emissions reduction and durability by understanding and optimising concrete chemistry, and highlights the pressing need for a more efficient, streamlined assessment technique to swiftly pinpoint high-performance, low-carbon materials in the ever-evolving field of cement and concrete types. This paper describes a novel Python-based algorithm called "Panoramix" (v.1.0) to explore relationships among mix proportioning, durability performance, and environmental impacts, using thermodynamic modelling, grid search and random sampling, a novel durability prediction method, and life cycle assessment. This study validates the algorithm by applying it to CEM I binders. The chemical composition range of the modelled clinker is as follows: CaO, 64-70 mass%; SiO_2, 19-25 mass%; Fe_2O_3, 1-5 mass%; Al_2O_3, 5 mass%; SO_3, 0.5 mass%; CO_2, 0.5 mass%; MgO, 1 mass%; K_2O, 0.5 mass%; Na_2O, 0.5 mass%. 97g of clinker and 3g of limestone is added per 100g binder. Water to binder ratio is 0.4 and gypsum to binder ratio is 4:100.

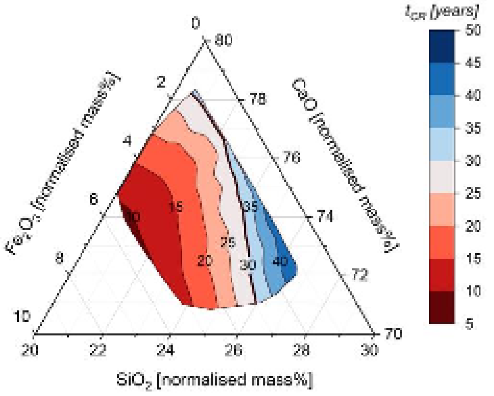

Figure 1. Ternary contour diagram of the freeze-thaw resistance indicator (the time to critical saturation degree, t_{CR} [year]) of CEM I based concrete as predicted by Panoramix, plotted against the bulk contents of CaO, SiO_2, and Fe_2O_3 in mass%, after 28 days of curing. An extent of reaction of 79% for Portland clinker is assumed and the total CaO + SiO_2 + Fe_2O_3 content is normalised into 100%. Cement binder: aggregate: air volumetric ratio is assumed to be 28%:68%:4%.

The result shows that CEM I binders tend to have higher freeze-thaw resistance at lower Fe_2O_3 content, as shown in Figure 1. These results indicate that a low-carbon and high freeze-thaw performance cement can probably be achieved by reducing Fe content in the kiln feedstock. A relatively high level of freeze-thaw resistance with t_{CR} (≥30 years, recommended for bridge deck and pavement concrete under freeze-thaw exposure conditions) is generally achieved at normalised Fe_2O_3 contents below 2% (within the bottom area in Figure 1 that is bounded by the bold black line), corresponding to unnormalised Fe_2O_3 contents in clinker of approximately < 2.2%. Climate change impact per 1 m^3 concrete is 282 kg CO_2-eq.

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EFFECT OF CALCINATION OF GRANITE ASH RAW MATERIAL IN MECHANICAL PROPERTIES AND MICROSTRUCTURAL STUDY OF GRANITE ASH-SLAG BLENDED HARDENED PASTE

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ABSTRACT

The present study investigates the calcination of granite ash as a pre-thermal treatment to enhance geopolymerization through alkali activation. An experimental program is performed to compare the compressive strength of calcinated & un calcinated granite ash geopolymer concrete to distinguish the role of calcination. 75% of calcinated & un calcinated granite ash's binder content showed an increase of 36% in strength at day 28 of curing. This result provides evidence for the improved geopolymer reaction. The results also show that the reactivity is at its highest when GGBS is replaced with granite by 50% compared to 75% for both calcinated and uncalcined granite samples. OPC samples is used as a control. The calcinated and uncalcined granite ash's binder content showed an increase of 36% in strength at day 28 of curing. This result indicates the improvement of geopolymerization reaction as more binder has been formed using pre-treated granite ash raw material. To understand the effect of calcination, the granite particle size before and after treatment is observed in SEM with the morphology showing a reduction in particle size that leads to more surface reaction to alkali. To validate the results between calcined granite samples, CGA50S50 confirmed more potential reactivity than CGA75S25 and OPC-Control, due to the activation of Ca in Ground granulated blast furnace slag will get reacted first and formed the C-A-S-H binder before proceeding with the formation of N-A-S-H binder from granite aluminosilicate. Overall, the experimental results reveal that the quality of the geopolymer enhances as the calcination temperature is applied. Via calcination, the order of crystalline structure in granite ash has been interrupted and this disordered structure favours the alkali activation of granite ash in forming geopolymer.

Introduction: The scarce supply of Fly ash and GGBS as an alternative binder in the UK [1] has led to an interest in studying other types of more available waste like granite. Granite has a similar chemical composition to fly ash class F which is silica 65% and alumina 14%, hence the study of using it as an alternative binder. In this study, granite is used as a partial binder of GGBS activated with a mixture of sodium hydroxide and sodium silicate. The name GA50S50 denotes granite ash 50% with Slag 50% and the letter C represent the Calcined of related mixtures. The compressive strength is carried out in accordance with EN 12390-3 with a load rate of 0.4MPa/s of days 7, 14 and 28 is presented in Figure 1 and the compressive strength of the mixtures after 28 days is displayed in Figure 2.

Results:

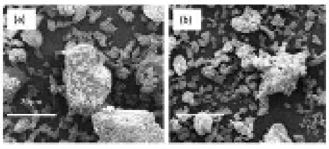

Fig.1 Micrographs of starting raw materials (a) granite ash and (b) granite ash pre-calcined at 800˚C for 3 hours observed in SEM.

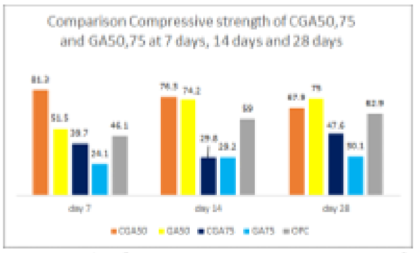

Figure 2: Compressive strength of alkali-activated granite-slag hardened paste

Discussion and conclusion: Figure 1 shows clear comparison of untreated and treated. Uncalcinated granite ash has a larger particle size and is less powdery than the calcinated starting raw material. The lower size of granite particles prepares for more surface to be reacted with the alkaline activator. The intense temperature involved did not just decompose the structure, and reform it but also reactivate the inert minerals. Pre-calcined granite ash exhibits higher polymerization activity that is made known in the compressive strength shown in Figure 2 compared to ordinary granite ash used in synthesizing the geopolymer. Calcined 50% granite and 50% slag (CGA50S50) has achieved 67.9 MPa at 28 days, surpassing the strength of OPC as control.In summary, calcination as pre-treatment of granite ash has prepared it to become a better binder compared to uncalcinated granite.

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MECHANICAL PERFORMANCE MODELS FOR CONCRETE AND CEMENT PASTE: A REVIEW

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ABSTRACT

Concrete usage is responsible for 9% of the total anthropogenic CO2 emissions. Most of these emissions are caused by the production of Portland cement. For this reason, there is a research interest in alternative types of cement and it is likely future concrete mixtures will have more variable compositions than what is common today. A promising option is to substitute Portland cement with larger quantities (up to 100%) of industrial by-products called supplementary cementitious materials (SCMs) (Shah et al., 2022).

Nowadays, mixture specifications procedures (e.g. ACI committee 212) and performance prediction formulas (e.g. Abram's rule) are empirical: based on the century-long experience with Portland cement concrete. This implies they do not work for concrete formulations outside their original calibration. Consequently, they are not helpful during research of new concrete mixtures and they will not be flexible enough to cope with the foreseen mixtures' variability.

Given this background, we aim to review models which aim to predict the evolution of strength, stiffness and creep of concrete (and cement paste) given the mixture specifications. Specifically, we will discuss how these models work, their performance and their limitations. Additionally, we propose potential improvements.

Performance prediction models, which essentially attempt to simulate the processing-microstructure-property relations for cement-based composites, should help develop less polluting materials by reducing the number of necessary experiments. Routine mixture proportioning and structural optimization are other possible applications.

A single model, which has as inputs the mixture specifications and as an output the mechanical properties, is the summation of 2 different components: a hydration model and a micromechanical model. The first aims to predict cement's paste microstructural evolution given the mixture specifications as input. The second computes the mechanical properties of cement paste (or concrete) based on their microstructure. We will mostly focus on the micromechanical models. These can be split into analytical (or semi-analytical) and computational models. Both types rely on continuum mechanics. Analytical models are, generally speaking, much faster but less accurate than computational ones. We will only mention contributions that use machine learning or empirical formulas.

Micromechanical models that explicitly consider cement's paste microstructure (micrometres scale) are approximately 20 years old (Bernard et al., 2003; Haecker et al., 2005). Mesoscale models (millimetres scale), which consider cement paste as a homogeneous medium, are older. The advantage of the newer models is that it is not required to recalibrate cement paste properties to deal with different cement chemistry, mixture specifications and hydration degree. New experimental techniques like nanoindentation played a major role in this transition to smaller length scales of observation. Regardless, it is usually possible to use mesoscale models with microscale ones in a 'multiscale homogenization' procedure. The effect of the shape and type of aggregates is usually studied at the mesoscale.

The vast majority of analytical and computational models can predict concrete and cement paste's elastic properties quite reliably. However, not all models can deal with different cement compositions. Moreover, some of them do not behave well at early stages of hydration. There is less work on strength and creep. The best analytical strength model applies to Portland cement only (Königsberger et al., 2018), but in the last three years, promising computational approaches have been developed. Moreover, there is an increasing interest in multiphysics models.

Given the large number of contributions in this specific field (more than 80 publications), an extensive benchmark is necessary.

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DEVELOPMENT OF CEMENT ENCAPSULANTS FROM NATURALLY ABUNDANT SUPPLEMENTARY CEMENTITIOUS MATERIALS

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ABSTRACT

Nuclear energy provides clean energy but also produces radioactive waste which is damaging to the environment and human health, requiring very careful disposal. Radioactive waste is categorised into three classifications; Low-Level Waste (LLW), Intermediate-Level Waste (ILW) and High-Level Waste (HLW). ILW and HLW need long-term management and are typically dealt with by solidification within suitable materials. Cement is the most commonly used material for the solidification of LLW and ILW. It has been used the longest and has high mechanical strength, a stable structure and low permeability of gas and liquid, and is easy to operate and low cost. The strength, permeability and workability all need to be optimised specifically for this use[1].

Supplementary cementitious materials are materials added to cement to lower costs, improve end-product properties and minimise the carbon footprint of production.The blending of SCMs with Portland cement can complicate the hydration process. The kinetics of the SCM reactions depend on the chemical composition of both the SCMs and the reactive solution. Different hydrates can be formed during hydration, which can influence the strength and stability of the final product[1,2]. The most commonly used are fly ash and blast furnace slag. However, these are running in short supply, necessitating the use of more naturally abundant materials. To be able to use alternative SCMs to contain radioactive material, specifications must be developed from the characteristics observed in cements made with these.

Calcined sedimentary materials are effective for use as SCMs. High-purity calcined kaolinite clay, or metakaolin, has often been used as such, and the calcining of other clays is of significant interest. Metakaolin, for instance, undergoes a pozzolanic reaction with portlandite solution, to create a C-(A)-S-H phase, stratlingite, and AFm type calcium aluminate hydrate, refining the pores. The Ca/Si ratio is also observed to decrease with clay content, increasing the strength of the final product [3]. Limestone is commonly used as a filler for cement clinkers. It can improve the packing density if it is finer than the cement particles and reacts with the aluminate phases of clinker, the latter leading to a retention of ettringite. The addition of limestone also provides nucleation sites for C-S-H and increases the shearing rate. These enhance the nucleation of C-S-H and enhance the hydration rate.

Chemical reactions of limestone have been shown to impact alkalinity, humidity, and volume stability but studies have found mixed results and what effect this has and why[2].
Calcined clays, Limestone, and a combination of the two are all proposed alternative SCMs, but these will affect the specifications needed for the containment of radioactive waste. This work will look at how the properties of cement are changed by the aforementioned additions and how best to make these to be used for the encapsulation of radioactive material.

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FIBRE-INDUCED CARBONATION OF CEMENT PASTES UNDER AMBIENT CONDITIONS

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ABSTRACT

Concrete's vast usage significantly contributes to global CO_2 emissions despite its low carbon footprint per unit mass. Carbonation curing of cement-based materials, a promising carbon capture, utilisation, and storage (CCUS) approach, could potentially sequester a substantial portion of these emissions (Pamenter & Myers, 2021). However, achieving fast and efficient carbonation in dense concrete elements under economical conditions (CO_2 concentration <20 vol.%, ambient temperature and pressure, less than a few days of carbonation) remains challenging. This study introduces an innovative technique: embedding natural fibre strings in cement pastes to enhance CO_2 uptake during carbonation curing. The aim of this research is to investigate fibre-induced carbonation mechanisms and to introduce a novel image analysis procedure for carbonation profile assessment.

Natural fibre strings, comprising jute, hemp, cotton, and wool, were fixed in 15 ml polyethylene centrifuge tubes and embedded within a CEM I 52.5N Portland cement paste (w/c = 0.4). Following 24 hours of setting and hydration, the samples underwent carbonation curing for durations ranging from 1 to 7 days under specified conditions: 20 vol.% CO_2, 25°C ± 0.5°C, 64% ± 2% RH, and ambient pressure. Disks were extracted from varying depths (0 mm – 50 mm) and sprayed with phenolphthalein. An image analysis method, based on colour deconvolution (Ruifrok & Johnston, 2001) and overflow segmentation (Wong, Head & Buenfeld, 2006), was developed to separate carbonated and uncarbonated zones. After the designated carbonation period, carbonation profiles were evaluated qualitative and quantitatively by the proposed image analysis, thermogravimetric analysis (TGA), X-ray Diffraction (XRD) and Fourier-Infrared Transform Spectroscopy (FTIR);The findings from the image analysis were compared with the TGA results for validation.

Carbonation depth tests delineated two distinct mechanisms. Without fibre strings, CO_2 diffusion in specimens is surface-limited, whereas the inclusion of natural fibres, especially hemp, enables deeper CO_2 penetration. Image analysis accentuated hemp fibres' superior CO_2 induction capabilities. In the vertical carbonation profile, reference samples displayed a 0.94 mm carbonation depth over 7 days. The inclusion of hemp fibres made carbonation fronts detectable even at 50 mm depth at 3 days of CO_2 curing; after 3 days of exposure, the carbonation rim continued to grow but at a decelerated rate, reaching a near-plateau. Moreover, the results from TGA indicated that at the surface exposed to CO_2, specimens were fully carbonated, irrespective of fibre inclusion. For disks at depths between 10 mm and 50 mm, reference samples showed minimal to no carbonation. In comparison, hemp-embedded samples revealed deeper and more consistent carbonation from 10 mm to 50 mm. Within three days of curing, the CO_2 uptake at 10 mm depth increases from 5.30% to 14.74% with the addition of hemp fibres. An excellent agreement is established between the values obtained from image analysis and TGA, albeit with the former typically underestimating the degree of carbonation. XRD and FTIR results demonstrates similar patterns while confirming calcite was the major polymorph of the precipitated calcium carbonates.

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SUSTAINABILITY ASSESSMENT OF BAUXITE RESIDUE REUSE APPLICATIONS: A COMPARISON OF CEMENT AND CLAY BRICK PRODUCTION

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ABSTRACT

Bauxite residue (BR), commonly referred to as red mud is an important by-product from the processing of bauxite to aluminium hydroxide via the Bayer process which is a critical stage in aluminium production. The waste constitutes a significant environmental challenge due to the substantial volumes generated, with approximately 1.23 tonnes of BR generated for every tonne of alumina processed on a global scale. The cumulative effect has resulted in an extensive BR stockpile (approximately 4 billion tonnes) which are distributed in various designated storage facilities worldwide. As demand for aluminium grows, storage spaces decrease, and the ever-present environmental risk associated with large scale BR storage remains. There is a need to identify alternative avenues to traditional storage. An appealing avenue is the utilisation of BR into applications such as cement and brick which can consume significant amounts of the material and make use of its properties. To assess the environmental performance of this approach, this study employed life cycle assessment (LCA) to provide environmental insights into two specific BR reuse applications, the manufacture of BR-based cement and brick and compared them with their conventional counterpart processes.

A cradle-to-gate approach was adopted making use of the ecoinvent 3.9.1 database for the background data needed to develop the life cycle inventory, with the open source LCA software Activity Browser 2.8.0 used for modelling. The functional unit chosen for this study was the reuse of 1kg of dry BR for the specified applications. To model cement production it was assumed that co-calcination of BR (57.13%) and kaolin (42.87%) replaces 30% of the clinker used in ordinary Portland cement (OPC) while for the manufacture of BR-based brick and in line with literature it was assumed that a combination of BR (20%), coal fly ash (58.80%), $Ca(OH)_2$ (17.20%), Na_2CO_3 (4%) and NaOH (5%) replaces conventional clay-fired bricks. The CML v4.8 2016 characterisation method was selected to perform the LCIA making use of all inherent method impact categories. A sensitivity analysis was conducted exploring the potential effect of varying BR composition on the environmental performance.

The outcome of this study quantitatively demonstrates that the utilisation of BR for cement and brick production has reduced environmental impacts in most of the assessed impact categories than their conventional counterpart technologies (OPC and clay brick). For cement production the BR-based cement has reduced environmental impacts in all categories except ozone depletion (39.34% higher). The observed disparity in the impact category can be attributed to the low influence of the clinker, a known significant contributor to the environmental footprint of cement production and higher weighting of kaolin, electricity, and natural gas. For brick production, negative environmental impacts were calculated in many impact categories, meaning that environmental impacts are reduced using the BR-based technology. For example, BR based brick production has a negative global warming potential value (- 6.25 $kgCO_2$-eq. / kg) indicating a net cooling effect. The incorporation of coal fly ash, which is a waste product from coal fired electricity generation is primarily responsible for the environmental benefit of BR based brick. Comparing the two competing BR reuse applications reveals that only in two (marine aquatic ecotoxicity and ozone depletion potential) of the eleven selected impact categories did manufacturing BR based brick exhibit a higher environmental burden than BR based cement production per kg of BR treated. This shows that considering BR utilisation strategies other than its use in cement may be preferable for reducing environmental impact. We expect similar conclusions may be obtained from the utilisation of other industrial by-products. This study represents an initial step towards mapping

the environmental impacts of utilising BR in suitable applications contributing to the goal of achieving sustainable alumina generation.

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USING REACTIVITY TESTS TO PREDICT PERFORMANCE AND SCREEN RESOURCES FOR CALCINED MIXED MINERAL UK CLAYS

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ABSTRACT

There is a need to decarbonise cement production, and supplementary cementitious materials (SCMs) is an effective means of doing this. However, supply of conventional SCMs is limited, so alternatives are being sought. Understanding the reactivity of these alternative SCMs is vital and many test methods are available for assessing chemical reactivity. Comparing different test methods helps us to better understand the reactivity of SCMs in cementitious systems (Ramanathan et al., 2020; Kasaniya et al., 2022). Here, the R3 bound water test (ASTM C1897-20, lime-mortar strength test (RILEM TC-267) and strength activity index test (BS 8615-1) were used to assess the pozzolanic potential of different calcined clays. Three calcined clays with varying kaolinite contents of 20% (CC-W), 50% (CC-F) and 70% (CC-IP) were evaluated.

For the R3 test, paste specimens were prepared according to ASTM C1897-20. Bound water contents were estimated using a laboratory muffle furnace after 7 days. Lime-mortar tests were conducted according to the RILEM TC-267 recommendation (Parashar et al., 2022); measuring the compressive strengths of three 50mm lime mortar cubes after 10 days. The strength activity index of the calcined clays was measured according to BS8615-1. Standard 40x40x160 mm mortar prisms were cast, replacing 25% of cement with calcined clays, and compressive strengths were measured after 28 and 90 days.

Figure 1 for these three values we can see that they satisfy the R3 bound water criteria for medium reactivity clays. Figure 2 shows that even a calcined clay with 20% kaolinite content clay was found to be sufficiently reactive.

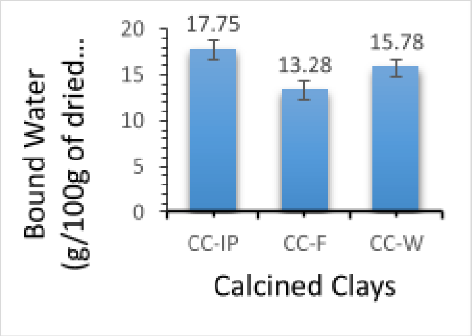

Figure 1: Values for R3 Bound Water Measurement for calcined clays at 7 days.

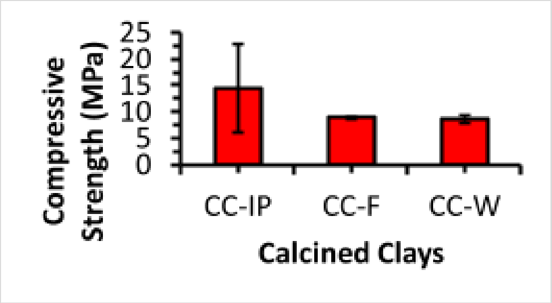

Figure 2: Lime mortar reactivity strength at 10 days

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INTRODUCTION TO MICROANALYSIS IN THE SEM FOR CEMENTITIOUS MATERIALS

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ABSTRACT

Microanalysis in the Scanning Electron Microscope (SEM) has been around for a long time and is routine in a lot of research areas. This work will show examples of the different techniques available within an SEM and how they can be useful for cementitious materials.

One of the most common techniques is Energy Dispersive X-ray Spectrometry (EDS/EDX), this technique works by collecting and detecting the x-rays that are emitted by the sample, during electron bombardment. Each element has a unique x-ray energy which the software can automatically identify and quantify. This can be visualised by overlaying individual chemical maps, together with the image from the SEM. This can be very useful to quickly identify phases and it's also been shown that EDS can quantify phase content with similar precision as XRD[1]. Figure 1 shows an example of an EDS spectrum, along with an EDS elemental map of concrete.

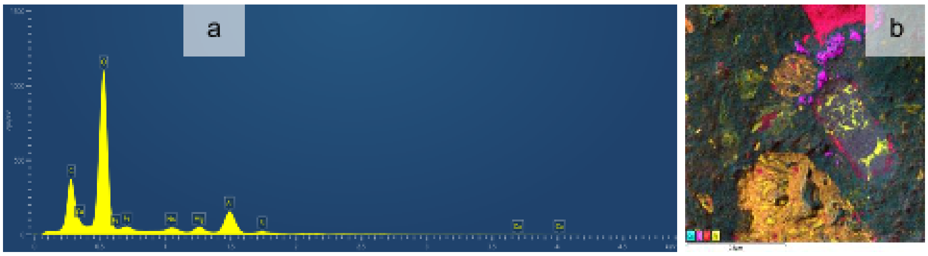

Figure 1. a) EDS spectrum of conrete with the corresponding EDS layered map (b)

Another good technique is electron backscatter diffraction (EBSD), which analyses the crystal structure of materials – how the atoms are arranged, how these crystal structures are aligned, the grain size and shape, along with localised strain analysis. EBSD works by diffracting electrons off the surface of the sample, which will cause a diffraction pattern (Kikuchi pattern) to be detected. Each type of crystal has a different pattern, and these patterns, along with EDS, can be used to identify what phases are present. Figure 2 shows an example of a Kikuchi pattern, along with an EBSD phase map of grey Portland cement[2].

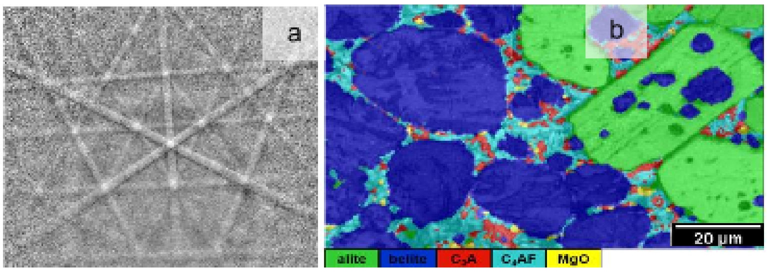

Figure 2. a) Kikuchi pattern of alite (20 kV, 1 nA, 180 nAms), and b) EBSD phase map of grey Portland Cement

A recent microanalysis technique within the SEM is Raman in SEM (RISE). Raman spectroscopy is an excellent complimentary technique to EDS, as it can show the compounds present, whereas EDS will show the individual elemental distribution. Raman spectroscopy works by vibrating bonds with photons and detecting the scattering events. For Raman, the scattering events that cause a

change in photon energy are what will be analysed. Different compounds will have unique Raman spectra which the software can automatically assign.

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MULTIMODAL ANALYSIS OF CONCRETE AND CEMENTITIOUS MATERIALS

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ABSTRACT

Concrete is the second most used material in the world and the production of cementitious materials generates a significant carbon footprint.[1] This is driving research into greener approaches for both the production of concrete and the material itself. For these approaches to be successful, the properties of the bulk material must match or improve current standards and the analysis of the internal chemistries of set concrete materials can help to understand these physical properties in more detail.[2]

Raman spectroscopy uses the inelastic scattering of photons to provide a spectral fingerprint of the material. This means individual components within a matrix can identified. Confocal Raman microscopy provides spatially-resolved Raman maps, meaning the distribution of chemically different components can be displayed visually. The RISE (Raman Imaging and Scanning Electron) system is the incorporation of a confocal Raman microscope within an SEM (Scanning Electron Microscope) environment. This grants users the ability to employ SEM imaging to aid with targeted Raman analysis in addition to conventional SEM based analytical techniques. Figure 1 displays the RISE system and imaging and analysis on a grain within a form of concrete.

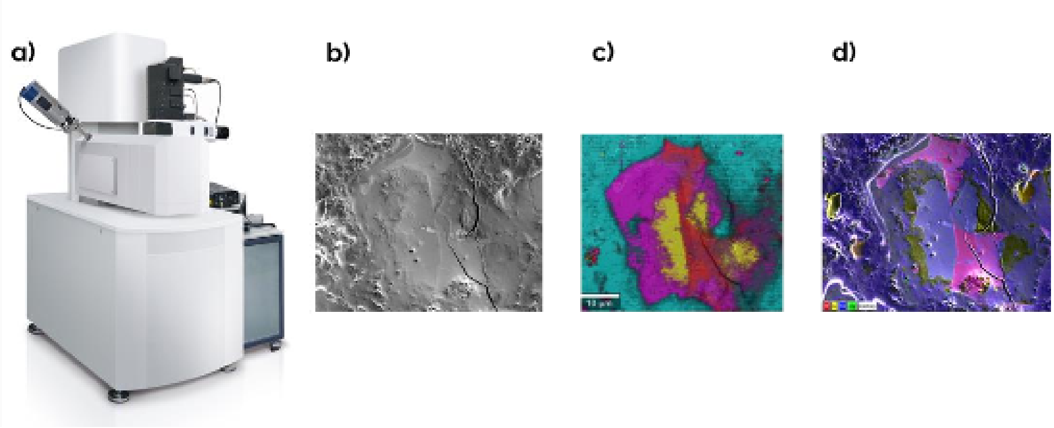

Figure 1 – a) The RISE-EDS system b) A backscattered electron image of concrete grain, c) the Raman map of the grain and d) the EDS map of the same grain.

When used in correlation, EDS (Energy Dispersive X-ray Spectrometry) and RISE analysis provides complementary information on the internal chemistries of the components within the mixture. Phases such as C_3S, C_2S and C-S-H can be identified and analysed, providing information on the degree of hydration of calcium silicate phases. Employing large area EDS mapping helps to provide a better understanding of aggregate distribution. Detailed comprehension of both calcium silicate hydration and aggregate distribution helps to provide a complete picture of the physical materials of the bulk property. This work will demonstrate the RISE-EDS workflow and the insightful information we can obtain for set concrete matrices without the need for destructive approaches.

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REACTIVITY ANALYSIS OF DIFFERENT MgO SOURCES FOR USE IN Mg-BASED CEMENTS

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ABSTRACT

Magnesium-based cements involve magnesium oxide (MgO) as the main raw material. The reactivity of MgO directly influences the rate of reaction and formation of hydration products, thereby impacting the physical and mechanical properties of these cements. This property is influenced by the chemical nature of the precursor used to produce MgO and the production conditions, such as calcination temperature and residence time in the calcination furnace, which modify the specific surface area of the material. In this study, two different sources of MgO were compared, including MgO obtained by calcining magnesium hydroxide $Mg(OH)_2$ at 850°C for 2 hours, and MgO obtained by calcining magnesite ($MgCO_3$) at 700 ºC. Analytical techniques included the measurement of the surface area by Brunauer, Emmett and Teller (BET), Thermogravimetry (TGA), X-ray diffraction (XRD), chemical reactivity evaluation by the citric acid neutralisation test, and hydration tests at room temperature and 80°C. Additionally, the morphology of the materials was observed using Scanning Electron Microscopy (SEM), and the impact on mechanical properties was evaluated through compressive strength tests at 7 days. The main objective was to characterise MgO for its application in MgO-based cements, specifically for Magnesium Silicate Hydrate (M-S-H) and Magnesium Oxysulphate Cement (MOS) mixes. The findings provide information for the appropriate selection of MgO in cement formulations based on its reactivity and mechanical performance.

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DETERMINING THE VOLUMETRIC RATIO OF HYDRATION PRODUCTS TO REACTED BLENDED CEMENT SYSTEMS BY THERMODYNAMIC MODELLING

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ABSTRACT

The hydration products of ordinary Portland cement (PC) are known to occupy approximately twice the volume of reacted cement. [1] The actual volumetric ratio (δ_v) can be derived from Powers and Brownyard's model [2] using the mass fractions of four main cement clinker phases (C3S, C2S, C3A and C4AF). However, the applicability of the value to blended systems, which are more complex in composition and involve latent hydraulic or pozzolanic reactions, remains largely unclear. This study analysed δv changes over time for 3 types of slag and fly ash using replacement levels of 20%, 40%, and 60% and w/b ratios of 0.4, 0.5, and 0.6. The phase assemblages of the binder systems were predicted by using the Gibbs Energy Minimization Software for Geochemical Modelling (GEMS) software, which was formulated by chemical thermodynamic equilibrium and incorporated into the CEMDATA18 database. [3–6]

Six series of PC cement data from the Powers and Brownyard Model were used to validate the accuracy of the estimated values of δ_v. The results showed that the volumetric ratio decreased rapidly before the initial setting of cement. However, it stabilised at a constant value of 2±0.2 after one day of hydration, closely matching that determined by Powers and Brownyard on well-hydrated systems. The δ_v of blended systems was found to exhibit a similar trend to the PC systems. Irrespective of the binder type, the volumetric ratios lie between 1.8 and 2.2. However, as the replacement level of SCM increased, a more significant decrease in the volumetric ratio occurred. This is due to the pozzolanic or latent hydraulic reaction of the SCM, which condenses the hydration products through the formation of additional C-S-H and C-A-S-H phases.

The volumetric results from GEMS were applied to determine the free w/b ratios between 0.25 to 0.5 of hardened slag-blended cement pastes analysed by backscattered electron microscopy combined with image analysis. The estimated w/b ratios and estimated slag replacement level are within ±5% of the actual values. Overall, this study has shown the viability of combining thermodynamic modelling, backscattered electron microscopy and image analysis for determining the free w/b ratios of hardened cementitious materials containing SCMs.

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POZZOLANIC REACTIVITY OF SUPPLEMENTARY CEMENTITIOUS MATERIALS DERIVED FROM WASTE FIBREGLASS

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Abstract

The utilisation of supplementary cementitious materials (SCMs) in concrete production has gained significant attention due to their potential to enhance both the sustainability and performance credentials of cements and concretes. This study focuses on investigating the pozzolanic reactivity of recycled powders derived from waste wind turbine blades, or glass fibre reinforced polymers (GFRP), as potential SCMs, which can add to the range of supplementary cementitious materials becoming more commonplace. The incorporation of such waste products into concrete aligns with the objectives of circular economy and resource conservation. This research also identifies a potential secondary route through which waste fibreglass may be recycled, this being a typically highly challenging, prohibitively expensive, and potentially environmentally damaging process.

The research methodology involved a comprehensive assessment of the reactivity of waste wind turbine blade powders. The chemical, mineralogical, and morphological composition of the recycled powders was investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to observe the removal of resin and chemical alteration, and thermogravimetric analysis (TGA) was employed to identify the decomposition temperature required for the complete elimination of resin. Residual polymer, which would typically impinge the surface and inhibit the reaction, was first removed from the fibreglass by heating the material to 600°C for 60 minutes before milling for 240 minutes to reduce the material to a fine powder. The pozzolanic reactivity was then evaluated through the standardised R^3 test methods and through observation of the compressive strength development, relative to conventional mortars.

The study revealed significant findings regarding the pozzolanic reactivity of recycled powders. XRD analysis indicated the presence of a significantly amorphous phase intermixed with quartz, gibbsite, and calcite. Based on the chemical composition of the material reported by X-ray fluorescence spectroscopy, it was identified that this amorphous phase could potentially be capable of reacting as a pozzolan. On milling of the powder, SEM micrographs indicated alterations to particle morphologies conducive to an increase in reactivity (decrease in size; increase in surface area), and these observations were validated using laser particle size analysis. Compressive strength tests were then performed on blended pastes to assess the reactivity of mixes incorporating recycled powders, and the results demonstrate a gradual increase in strength as the material hydrated, with a compressive strength which was competitive with that provided by a fly ash. The thermal output and bound water test findings corroborated the reactivity trends indicated through compressive strength testing, confirming the potentially enhanced early-age reactivity of the material through processing.

The findings underscore the viability of utilising recycled powders from waste wind turbine blades as supplementary cementitious materials. The demonstrated reactivity highlights their potential to contribute to sustainable, high-performance concrete. Incorporating such materials helps to address waste management challenges and aligns with sustainable construction practices. In conclusion, the investigation into the pozzolanic reactivity of recycled powders from waste wind turbine blades presents promising results. By employing XRD, SEM, TGA, compressive strength tests, and the R^3 test methods, this study provides valuable insights into the potential of these materials to act as effective supplementary cementitious materials. Further research can optimize their proportions in concrete mixtures and assess long-term durability performance, thereby significantly contributing to sustainable construction materials and waste utilisation.

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CARBONATION-INDUCED CORROSION IN LOW CO_2 EMISSION CONCRETE

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ABSTRACT

Global cement production results in significant carbon dioxide (CO_2) emissions, impeding the international effort of achieving net-zero by 2050. Therefore, there is an urgent need to develop low-carbon concretes which are more sustainable and durable. Low-clinker cements involving the use of high replacement levels of supplementary cementitious materials (SCMs) are one promising solution.

However, such cement systems are more prone to carbonation than ordinary Portland cement systems due to the lower calcium content and consumption of $Ca(OH)_2$ by pozzolanic reaction, thereby reducing the pH buffering capacity. When the pH of the pore solution is lower than the depassivation threshold of steel reinforcement (around 9.5), the protective passive film on the steel surface will lose its thermodynamic stability, enabling corrosion to initiate. The accumulation of corrosion products induces stresses at the steel-concrete interface, leading to cracking and spalling of the concrete cover.

The concerns related to a greater risk of carbonation-induced corrosion in low-clinker cementitious systems present a major barrier to their wider industry uptake. This PhD project aims to study the relationship between the carbonation of low-clinker concretes and steel corrosion kinetics, including the impact of pore solution chemistry, moisture retention, and microstructure of bulk matrix and steel-concrete interface (SCI). The project consists of four main parts:

I. Pore solution analysis: Pore solution chemistry (including pH and composition) and phase assemblage for a range of low-clinker systems will be determined as a function of binder type, age, and exposure in natural and accelerated carbonating environments. Thermodynamic modelling will be used to simulate the carbonation process of different blended systems. The results will be compared with corresponding pore solution data from experiments on paste samples. Experimental methods will include cold water extraction, pore water expression and 'wet carbonation' method.
II. Moisture retention studies: The deliverable of this task is moisture retention and distribution in different carbonated systems under saturated and partially saturated conditions. The relevant variables are binder type, degree of carbonation and exposure environment (wetting/drying). The study will focus on paste and mortar samples. Major experimental methods will include thermogravimetric analysis, dynamic vapour sorption and neutron radiography.
III. Microstructure of bulk matrix: This task evaluates the phase composition and pore structure of the bulk matrix for different binder types, degree of carbonation and exposure environment (wetting/drying), to further explain the mechanism of how carbonation impacts the moisture state measured in Task II and the related steel corrosion kinetics. Experiments will be performed on paste and mortar samples, using a range of methods including SEM-EDS, X-ray CT, X-ray diffraction, Raman microscopy, mercury intrusion porosimetry, and gas absorption-BET.
IV. Microstructure of steel-concrete interface: The microstructure gradients at the SCI will be quantified as a function of binder type, degree of carbonation and exposure environment (wetting/drying). This will complement Part III in answering the impact of carbonation on moisture state and steel corrosion kinetics. Experiments will be conducted on lab-prepared paste and mortar samples, and field samples from natural exposure sites or engineering structures. The results will help link the properties of laboratory and field-exposed structures and develop predictive relationships to enable practical applications.

Overall, this research seeks to unravel a more profound fundamental understanding that is essential for harnessing the full potential of environmentally friendly, low CO_2 emission concretes while concurrently safeguarding their long-term durability.

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ENVIRONMENTAL IMPACT OF 3D PRINTED GEOPOLYMERS VS. 3D PRINTED CONCRETES

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ABSTRACT

One major issue in the construction industry is excessive use of ordinary Portland cement (OPC), the use of OPC produces around 10% of the world's total CO2 emissions. Geopolymers are materials which share many properties with concretes including similar densities, strength, and hardness however the environmental impacts are greatly reduced. Geopolymers rely on a geopolymeric reaction, there are multiple stages to this reaction (stages can vary depending on precursor materials), first an Aluminosilicate is mixed with an alkaline activation to produce a geopolymer monomer, this monomer then reacts with alkali to produce a long range geopolymer system. Geopolymer technologies are developing rapidly, this project focuses on the 3D printability of green Geopolymer slurries. 3D printed concrete and geopolymer samples were tested for structural properties including compressive testing, tensile testing, and impact testing. Environmental impact was evaluated based on the environmental impact of used materials and the environmental impact of producing the samples. A 3D printable slurry with high amounts of recycled steel industry slags was developed, it was found that the geopolymer samples have similar structural properties to 3D printed concretes, however the geopolymer samples have much less environmental impact.

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WASTEREBUILT: A CIRCULAR APPROACH TO WASTE FOUNDRY SAND REUSE INTO THE BUILT ENVIRONMENT

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ABSTRACT

Globally, 113 Mt/year of cast metal are produced, generating 10-20 Mt/year of waste foundry sand (WFS). In the UK alone, 200,000 tonnes of WFS are disposed of via landfilling, challenging current efforts in tackling climate change and sustainable development. Concrete uses up to 90% of natural aggregate per tonne of concrete produced, including sand. The latter is the most extracted material in the world today, with up to 50 billion tonne/year of sand mined around the globe for construction.

This work examines preliminary results of the WASTEREBUILT project (EPSRC-IAA, Cardiff University), aimed at investigating the use of waste foundry sand (WFS) as a replacement for fine aggregate (sand) in concrete. Chromite and quartz WFS supplied by Weir UK was used. Portland cement CEM I was supplied by Dragon Alfa Cement UK.

Preliminary analysis on the WFS showed that both quartz and chromite sand was finer than standard river sand and contained less silicon but richer in metallic ions. Leaching tests showed that WFS released metals, but their chloride and sulphate content was within the environmental limits. Loss on ignition and total carbon analyses showed that the organic content and carbonaceous material were lower in the WFS compared to the river sand. pH and electroconductivity measurements of leachate from the sands suggested that the WFS would behave similarly to the river sand when used in concrete.

WFS was then used in concrete at different fine aggregate replacement levels (30 – 100% by weight) and tested for strength and durability. The mechanical performance was investigated at 28 days of curing, as well as water transport, and durability properties (freeze/thaw cycles exposure). While the overall compressive strength decreased with increasing WFS content, samples subjected to freeze/thaw cycles exhibited outstanding durability performance with respect to their water absorption capability.

Waste foundry sands, as a substitute for natural sands in concrete, can improve its properties. The study found that a full substitution rate is possible, and the resulting concrete is more durable and resistant to water and harsh chemicals. The results showed that compressive strength and tensile strength decreased as the substitution level increased due to the high water content and fineness of the sands. Thermal conductivity decreased with increasing substitution levels, but water absorption decreased at all substitution levels. Controlling the amount of water added to the mixtures containing WFS could increase strength, as the total water content used led to a to 100% chromite sand led to poor workability (failed slump test). Specimens containing high level of WFS also performed better under mechanical stress and showed less internal degradation due to its higher density and less porous structure. The study also conducted tests on the concrete's ability to withstand freezing and thawing cycles, which further boosted its mechanical properties.

Overall, using waste foundry sands in concrete can be a viable and beneficial alternative to using natural sands. This work suggests that WFS is an environmentally sustainable solution for both the cast metal industry and the construction sector, as it repurposes a material that would otherwise be disposed of into a raw material for durable concrete production.

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HYDCEM – A NEW CEMENT HYDRATION MODEL

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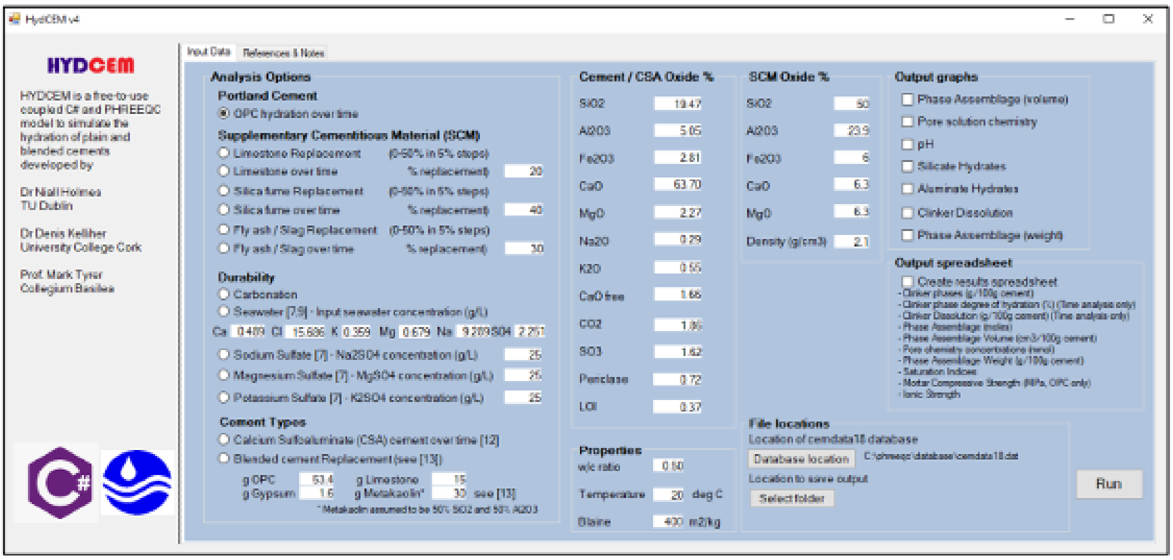
ABSTRACT

HYDCEM (HYDration of CEMent) is a free-to-use cement hydration model to predict the changing phase assemblage. It is written in the C# programming language, which assembles the input file (a 'script' in C#) in the correct syntax for the geochemical code, PHREEQC, which is called (using the iPhreeqc module) and runs the analysis to predict the physical and chemical evolution of the cement system.

There are several analysis options including OPC/CEM I hydration and supplementary cementitious materials such as limestone, silica fume, PFA and GGBS. The user can choose to run the analysis as a percentage replacement of cement or over time. In addition, users can analyse the effect of OPC/CEM I cement in several harsh environments such as carbonation, sulfate (sodium, magnesium and potassium) and seawater. Finally, it includes analysis of calcium sulfoaluminate (CSA) and metakaolin blended cements. A front-end image of HYDCEM is shown in Figure 1.



HYDCEM is a free-to-use coupled C# and PHREEQC model to simulate the hydration of plain and blended cements developed by

Dr Niall Holmes
TU Dublin

Dr Denis Kelliher
University College Cork

Prof. Mark Tyrer
Collegium Basilea

Analysis Options

Portland Cement

● OPC hydration over time

Supplementary Cementitious Material (SCM)

○ Limestone Replacement (0-50% in 5% steps)
○ Limestone over time % replacement) 20
○ Silica fume Replacement (0-50% in 5% steps)
○ Silica fume over time % replacement) 40
○ Fly ash / Slag Replacement (0-50% in 5% steps)
○ Fly ash / Slag over time % replacement) 30

Durability

○ Carbonation
○ Seawater [7,9] - Input seawater concentration (g/L)
Ca 0.489 Cl 15.686 K 0.359 Mg 0.679 Na 9.289 SO4 2.261
○ Sodium Sulfate [7] - Na2SO4 concentration (g/L) 25
○ Magnesium Sulfate [7] - MgSO4 concentration (g/L) 25
○ Potassium Sulfate [7] - K2SO4 concentration (g/L) 25

Cement Types

○ Calcium Sulfoaluminate (CSA) cement over time [12]
○ Blended cement Replacement (see [13])
g OPC 53.4 g Limestone 15
g Gypsum 1.6 g Metakaolin* 30 see [13]
* Metakaolin assumed to be 50% SiO2 and 50% Al2O3

Cement / CSA Oxide %

SiO2 19.47
Al2O3 5.05
Fe2O3 2.81
CaO 63.70
MgO 2.27
Na2O 0.29
K2O 0.55
CaO free 1.66
CO2 1.86
SO3 1.62
Periclase 0.72
LOI 0.37

Properties

w/c ratio 0.50
Temperature 20 deg C
Blaine 400 m2/kg

SCM Oxide %

SiO2 50
Al2O3 23.9
Fe2O3 6
CaO 6.3
MgO 6.3
Density (g/cm3) 2.1

Output graphs

☐ Phase Assemblage (volume)
☐ Pore solution chemistry
☐ pH
☐ Silicate Hydrates
☐ Aluminate Hydrates
☐ Clinker Dissolution
☐ Phase Assemblage (weight)

Output spreadsheet

☐ Create results spreadsheet
- Clinker phases (g/100g cement)
- Clinker phase degree of hydration (%) (Time analysis only)
- Clinker Dissolution (g/100g cement) (Time analysis only)
- Phase Assemblage (moles)
- Phase Assemblage Volume (cm3/100g cement)
- Pore chemistry concentrations (mmol)
- Phase Assemblage Weight (g/100g cement)
- Saturation Indices
- Mortar Compressive Strength (MPa, OPC only)
- Ionic Strength

File locations

Location of cemdata18 database
C:\phreeqc\database\cemdata18.dat
Location to save output

Figure 1 HYDCEM front end

Several graphical outputs are available to view the results including phase assemblages, pore solution chemistry, pH and clinker dissolution. The data from each simulation can also be downloaded into a MS Excel spreadsheet for further analysis and formatting. HYDCEM employs the Cemdata18 thermodynamic database and is based on the authors' published work in the area.

The software is available to download from the authors website (www.hydcem.com) along with other software for cement-based analysis. To date, the software is being used in 25 countries and an updated version (v4.01) is under development to include additional features such as changing C-S-H Ca:Si ratio, heat of hydration and improved computational efficiency.

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INVESTIGATING THE INFLUENCE OF LAGOON FLY ASH AND ACTIVATORS ON THE PROPERTIES OF GEOPOLYMER COMPOSITES BASED ON GROUND GRANULATED BLAST FURNACE SLAG

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ABSTRACT

As a commonly used building material, Portland cement has many advantages, including but not limited to strength, durability, and diverse application scenarios. This versatile material finds extensive use in structural concrete for diverse infrastructural features including bridges, dams, and various edifices, in addition to its role as masonry mortar for the construction of brick, stone, and masonry units. The contemporaneous trajectory of urban expansion and construction endeavors substantiates the incremental augmentation of Portland cement production.

However, the considerable-scale manufacture of Portland cement bears concomitant environmental implications, primarily emanating from the substantial emission of carbon dioxide (CO2), which significantly contributes to the phenomenon of global warming. Moreover, the production of Portland cement necessitates elevated temperatures for the generation of clinker, thereby incurring substantial consumption of energy, predominantly sourced from coal and natural gas reserves. This combined context of production parameters and energy requisites engenders air pollution and the depletion of non-renewable resources, engendering the pursuit of alternative materials with enhanced ecological attributes.

The emergence of geopolymer materials as a prospective substitute for conventional Portland cement has been under consideration since the 1980s, owing to their notable strength characteristics and diminished CO2 emissions. Various geopolymer systems have been subject to scrutiny, among which the utilization of alkaline activators, such as sodium hydroxide and sodium silicate, to activate the reaction of ground granulated blast furnace slag (GGBS) and fly ash (FA) systems is prevalent. The reactivity intrinsic to GGBS and fly ash culminates in the formation of calcium silicate hydrate (C-S-H) and alumino-silicate gel matrices, ultimately enhancing microstructural densification, mechanical strength, and durability. This paradigmatic framework not only engenders materials showcasing attributes approximating or surpassing those of Portland cement but also affords a means of repurposing industrial waste.

The present study endeavors to assess the potential viability of a cementitious system encompassing ground granulated blast furnace slag (GGBS) and lagoon fly ash (KLFA) sourced from the Kilroot power station in Northern Ireland, as an eco-conscious alternative to Portland cement. KLFA is an offshoot of coal-fired power station residues, typically relegated to long-term containment within lagoons or waste repositories. Notably, scanning electron microscopy (SEM) analysis reveals distinctive particle clusters of varying morphologies and sizes, with visible C-S-H constituents. Evidently, prolonged exposure to outdoor conditions, including the corrosive influence of soluble salt vapors, has induced substantial chemical and physical alterations in KLFA, concomitantly incorporating numerous impurities that may detrimentally influence its use in geopolymer synthesis. Consequently, KLFA is generally perceived as a low-grade fly ash.

This study is devoted to activating the geopolymer system composed of GGBS and KLFA by different activators, taking the geopolymer composed of pure GGBS as the reference standard. The principal objective is to probe the impact of activator selection and lagoon fly ash incorporation on the functional characteristics of the geopolymer framework. The GGBS-KLFA ratio is set at 9:1, with three activators employed, namely Na2O, sodium silicate, and sodium sulfonate. Compressive strength tests demonstrate that samples treated with sodium silicate as the activator and supplemented with KLFA exhibit superior strength, culminating in a 28-day mortar strength of 59.5

MPa. This compares favorably with the pure GGBS group under identical conditions, which achieves only 58.0 MPa. The findings underscore the capacity of KLFA-treated geopolymer systems to enhance mechanical robustness, reinforcing the potential utility of this alternative material to substitute or complement conventional Portland cement.