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Proceedings from British Lime Association UK-Lime Research Symposium 2021

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Welcome from the British Lime Association

In October 2021 academics, industrialists, and early career researchers from across the UK gathered online to share their research into lime. The range of topics presented was astounding; highlighting the importance of lime in a wide range of applications to society now, and throughout the ages, whilst also allowing a glimpse of a few of the possibilities for the future of lime manufacturing.

We would take this opportunity to thank all the speakers for being involved in lime research and for their work in preparing their presentations and the excellence of their contributions.

We would also thank all the delegates who joined the symposium for their interest in and contribution to the event, as well as anyone who didn't attend on the day and has subsequently taken the benefit of the recording of the event. We would also thank all those behind the scenes who facilitated the event.

The British Lime Association is delighted to publish these selected papers that were presented at the Symposium.

The thriving research community that made the Symposium possible is the tip of the iceberg, both in the UK and internationally. There is of course UK research on lime related topics that was not presented at the Symposium, and it is hoped that making the suite of information shared with Symposium delegates available, will encourage other researchers to build connections and perhaps establish research communities active in lime research.

For more details on the Symposium, including arranging access to the recording of the day's presentations, please contact the British Lime Association by email: *bla@mineralproducts.org*. You can find out more about the British Lime Association on our website: *www.britishlime.org*.

The British Lime Association is part of the Mineral Products Association, the trade association for the aggregates, asphalt, cement, concrete, dimension stone, lime, mortar and silica sand industries – *www.mineralproducts.org*.

Contents

Extracting Minerals . . . Manufacturing Products . . . Supplying Markets

The Importance of Academic and Industry Collaboration in a Changing World

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INTRODUCTION

There is no doubt that Industry and academia are different. They are different in the goals underpinning their existence, in the way they achieve their aims, in the way they measure success. They are different in the way they innovate and in the way they adapt to an ever-changing world.

These differences are, however, not to be considered as 'ranking differences', that can be used to claim the predominance or importance of a sector over the other. Diversity, in this context, should instead be interpreted as *the awareness that each sector has its own distinctive traits.* As such, in this context 'diversity' should be interpreted as a synonym of *richness not as a threat* since, as Darwin suggested, *"productivity increases with species diversity".*[1] Therefore in an ever-changing world, as the one we live in, diversity should be considered an advantage, not a limitation.

However, if industry and academia – with all these differences – have something in common, it is their interest for research. Industry relies on research for product innovation and, therefore, for new income generation; Universities develop research to lay the foundation of major advances, to generate impact, and to offer students unique academic and career opportunities.

Of course, academic research and industrial research are different. In fact, it is generally accepted that academic institutions tend to develop more basic or *blue-sky* research, whereas the industry tends to develop applied research. Academic research looks more at the principles behind some facts, whereas industrial research looks at the practical applications of these facts (e.g., a product, a service). Timescale for impact of academic research tends to be longer than for industrial research, and also industrial research is developed within *Research and Development* (R&D) departments that requires skills (in particular the 'Development' side) that are not commonly part of academic curricula (i.e., exceptions are some University taught Business programmes).

Because of these differences, achievements and productivity in the research activity of the two sectors cannot really be compared. There are claims that, currently, the best research is done in industry, for instance because of the equipment available that can be newer compared to the one available in universities. This may be true in some cases (i.e., within big companies capable of heavily funding their R&D department), but it is not always the case, in particular with Small and Medium Enterprises (SME), or with some very specialised knowledge or equipment that may be available only within academic institutions.

THE REASON FOR COLLABORATING

What is sure is that the best results in terms of research activity for both entities (i.e. industry and academia) are achieved in situations of complementarity. That is, when industry and academia work together to develop *synergies that produce combined effects greater than the sum of their separate effects*. This is the reason why industry and academia should promote collaborations.

Collaborations between Universities and private or public companies enable both entities to sustain growth in their areas: if companies can make use of university research for product innovation (in particular, in highly competitive markets), Universities can gain prestige through increased external research funds and through impact.

Remarkable examples of successful collaborations between industry and academia are (to mention just the most recent and popular synergies) all COVID-19 vaccines that were developed by private pharmaceutical companies in a very short time thanks to the basic research carried out by academic institutions.

Importance of academic and industry collaboration in the current world is clearly highlighted by Phil Baty, Chief Knowledge Officer of the Times Higher Education who, in a THE Consultancy report published in November 2020, wrote: *"[THE] partnerships between Universities and Industry will be vital as nations seek to re-build their economies after the devastation of the pandemic".*[3] Within the same report it is also mentioned that: *"An area that continues to be high up the agenda of policymakers and university leaders is university-industry links and so called "knowledge transfer". A university's ability to help industry with innovations, inventions and consultancy has become a core mission of the contemporary global academy and is generally supported and encouraged by governments".*[4]

A HUMBLE BUT EXTREMELY USEFUL MATERIAL

The *UK-Lime Research Symposium* is an important opportunity for industry and university to meet and discuss their research activities on a quite 'humble' but extremely useful material: lime. Lime does not make into the news as graphene does in these years, is not as cool as the 'geopolymers', and its 'nano' version is barely known even to the specialists. Nevertheless, lime is and has been an extremely important material for mankind.

In 2014 it was estimated that, *"although lime products are rarely directly sold to consumers, the average EU citizen indirectly consumes around 150 g/day of lime products".*[5] It is usually unknown to the general public that lime has a role in most of the food we eat and in a variety of materials we come across every day. Lime is used in the production of butter, to reduce acidity of the cream separated from the whole milk. It is a main ingredient of a common type of baking powder, monocalcium phosphate. It has a vital role in the production of sugar from both, sugar cane and sugar beets, where it is used for pH correction and to remove impurities and colour from the sugar solution. Lime is used in the controlled atmospheric storage of fruit and vegetables, where bags of hydrated lime are placed on racks in the storage room to absorb CO_2 that exudes from ripening fresh produce. It is used in corn production where the harvested corn is first soaked in milk-of-lime before its conversion to cornmeal.[6] Every piece of paper is treated with lime as a causticizing agent. Lime is used to clean wastewater, preparing drinking water, removing acid gases from flue gases and enhancing soil stability. Lime products are important in the steel industry and

for the production of construction materials, paints, plastics as well as cosmetics, rubber, and glass.[7]

As a comparison, cement, which is the 2nd most consumed material in the world after water[8], is mostly used for producing mortars and concrete.

THE UK-LIME-RESEARCH SYMPOSIUM

The *UK-Lime research symposium* represents an important action from the industry to seek and promote collaborations with the academic world on a 'humble' but important material that does not usually make the news. The fact that most of the oral presentations are from academics and that presentations from industrial researchers were planned to be delivered via video posters shows the willingness of the industry to listen to what academics have to say.

However, to make this communication even more effective, it is important to highlight some of the challenges that industry and academia face in developing research on lime:

1. A personal consumption of 150g/day of lime is equivalent to 54.7 Kg of lime per year per person. As a comparison, the per capita consumption of cement in 2020 was 521 Kg[9], equivalent to ten times the personal consumption of lime. A similar ratio emerges from statistics on lime production worldwide which is about 420 thousand metric tonnes, compared to the 4.1 billion metric tonnes for cement in 2020.[10] It is, therefore, possible to infer that, despite the more varied use of lime and its importance to our daily life, the lime market (and the related business) is much smaller compared to the cement ones (i.e. about 1/10th). This, of course, entails limited funds for research.

2. Lime production is a high-capital intensity industry that produces low-cost products: it has high operational cost and high cost of renovation. Revenue is volatile, the market is highly competitive and is currently more challenging than in the past, considering that the COVID-19 pandemic has reduced the revenue from the construction sector (which is an important source of demand for lime producers), and the steel industry (which is still the most significant single market for the sector) is facing serious international competition. Finally, the industry is subject to increasingly stringent environmental regulations that have already led operators to improve the energy efficiency of their manufacturing processes[11] and reduce their emissions, with increased manufacturing costs, as a result of the implementation of the UK Emissions Trading System.

3. From an academic perspective it is clear that:

   a. Research on lime is fragmented and scattered among various academics in different UK institutions. Research on lime at academic level can be of the highest quality (e.g. EPSRC grant *'Experimentally verified atomistic modelling of lime in construction materials,'* led Dr Richard Ball from the University of Bath[12]) but is generally funded through individual grants that last a few years and then struggle to find the continuity that would be necessary to produce a more relevant impact.

   b. A substantial amount of academic research on lime focusses on the construction industry, although other topics (e.g. lime in asphalt) seems to gain momentum.

   c. In the UK there is no main centre for research on lime as, for instance, exist at the Universities of Leeds and Sheffield for cement.

   d. At European level, currently, the SUBLime project (SUstainable Building Lime applications via Circular Economy and Biomimetic Approaches) is probably the largest project publicly funded for research on lime.[13]

4. Finally, it is quite common to talk about lime as if it were a single product, but lime is not a single product. Of course, for chemists, 'lime' is just calcium oxide, but in the construction industry - as well as in other industries - lime is the name of a family of products in which every member has substantially different characteristics compared to the others. High calcium lime is different from Magnesium lime which, in turn, is different from any natural hydraulic lime and this entails that dedicated research projects should be necessary to investigate each of these materials.

AN URGENT NEED FOR COOPERATION

In such situation it is obvious that there is urgent need for cooperation and synergy between academic institutions and private and public companies. Any research that can help create new markets (e.g. lime in asphalt) or to develop a low-cost solution that can help by improving the characteristics of the materials already produced (e.g. the use of organic molecules to modify the characteristic of portlandite crystals), or solutions that can help improve the carbon footprint of the industry (e.g. carbon capture for kilns, or the switching to low emission fuels, or the production of slaked lime without CO_2 emissions) would be extremely beneficial to the industry and, in turn, to the University. Furthermore, academia should also collaborate with industry in other areas of activities related to lime such as the Health and Safety of the industry, as demonstrated by a collaboration between Singleton Birch and Hull University for which a video poster was presented in this symposium.

CONCLUSIONS

Industry and academia are different, but they share a common interest in research for which they can - and should - create synergies (with the aim to produce combined effects greater than the effects of individual efforts). Lime is a 'humble' material that is usually overlooked (and it has been overlooked for several decades now) that plays an important role in our daily life and therefore is the perfect 'ground' for synergies.

However, effective synergies can only stem from the knowledge and understanding of the needs and characteristics of the 'other' and the best way to know and understand 'the other' is through communication. The *UK Lime research symposium* organised by the British Lime Association is a rare occasion where industry and academia gather to communicate. Let's hope that one day this symposium will be remembered as the event that started a new era in the research on lime.

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[10] STATISTA. 2021. *Lime production worldwide from 2010 to 2020 and Cement production worldwide from 1995 to 2020*. On-line. Accessible at *www.statista.com/statistics/1006040/production-of-lime-worldwide/ and at www.statista.com/statistics/1087115/global-cement-production-volume/*. [Accessed on 23/02/2022]. It is important to point out, however, that revenue of cement manufacture in the UK in 2020 was only double the revenue for lime and plaster manufacture: 549 million US dollars vs. 205 million US dollars.

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Can Lime be Used to Reverse Climate Change?

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ABSTRACT

It is widely agreed that alongside emission reductions, CO_2 will need to be removed directly from the atmosphere and stored for long periods of time. Carbon dioxide removal (CDR) technologies aim to tackle this issue. An example of this is mineral carbonation, where CO_2 from the atmosphere is reacted with alkali metal oxides, such as magnesia (MgO), lime (CaO), or their hydrated equivalents, to form stable carbonates. Until recently, most of the research on CaO carbonation has focused on 'calcium looping' involving the reaction of CaO with flue gas concentrations of CO_2 at high temperatures for emissions reduction. Alternatively, carbonation can be performed using CO_2 in air for the purpose of CDR. However, less is known about what controls the rate and extent of carbonation at these conditions, which are essential for process optimisation and scale-up.

INTRODUCTION

Increasing anthropogenic carbon dioxide (CO_2) emissions are the primary cause of global climate change and its subsequent negative impacts[1]. Given that CO_2 is long-lived in the atmosphere, to prevent climate change net-zero emissions must be achieved[2], whereby anthropogenic emissions are reduced, and residual emissions are balanced by the removal of CO_2 from the atmosphere[3, 4]. The necessary scale of CO_2 removal (CDR) may be around 10-20 Gt of CO_2 per year by 2050[5] with the aim of reaching the Paris Agreements goals of remaining below a 2°C temperature rise above preindustrial levels.

CDR approaches encompass a range of approaches which ultimately remove CO_2 from the atmosphere, these include terrestrial based methods (e.g. afforestation), marine management (e.g. blue carbon), anthropogenic materials (e.g. carbonation of lime), enhancement of ocean alkalinity (e.g. ocean liming), and direct air capture (DAC)[6]. To reach multiple Gt/yr of CDR it is likely that a portfolio of these methods will be required which may have advantages and disadvantages when deployed simultaneously[7]. This report focuses on CDR using the anthropogenic material lime (CaO), specifically the ambient carbonation of CaO.

CaO reacts with atmospheric CO_2 to form stable carbonate minerals, which is common in the use of lime mortars or renders[8, 9]. The reaction between CaO and air is spontaneous therefore no additional energy is required to incite this reaction. Most of the research on lime to date has focused on high temperature and high-pressure reactions, usually as a method of scrubbing CO_2 and sulphur from flue gases[10], conversely the mechanisms of this reaction in ambient conditions with low concentrations of CO_2 are not well characterised. However, the characterisation of the rates, extents, and kinetics of this reaction in ambient conditions will be essential to scaling up this technology.

THE REACTION OF LIME WITH AIR

CaO reacts with CO_2 to form stable carbonate minerals ($CaCO_3$) via the equation below (Eq. 1).

$$CaO(s) + CO_2(g) \longrightarrow CaCO_3(s) \quad \text{Eq. 1}$$
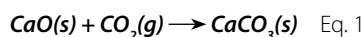
CaO carbonation at ambient conditions has been explored in a small number of experiments[11, 12], most of the work in the literature on 'ambient carbonation of lime' surrounds the ambient carbonation of lime mortars and renders specifically for the strengthening properties which come with carbonated lime mortars[13], which although bear some relevance do not offer information in the context of a powdered material for optimising a CDR technology. The factors which control CaO carbonation are humidity, temperature, partial pressure of CO_2, lime particle size, and supply of CO_2 to the lime particles.

METHODS OF INCREASING AMBIENT RATES AND EXTENTS

High temperature (350-800°C) and pressure (20-100% and 1-3 Bar CO_2) reactions of lime with CO_2 generally happen on the scale of seconds to minutes[14, 15], whereas in ambient conditions, where the concentration of CO_2 is considered dilute, the reaction time is slower generally occurring in weeks to months[11]. Although the former reaction is faster than ambient carbonation the energy requirements and source of CO_2 usually mean that the overall process would not be considered a CDR approach. The challenge for ambient carbonation is therefore how to increase this reaction rate in ambient conditions without emitting more CO_2 than captured during the process. This leads to technology ideas surrounding passive and low energy systems that can be scaled up.

Recent studies have suggested spreading metal oxides across land in piles/layers to carbonate with atmospheric CO_2[16,17], the thickness of the layers was suggested to range from 2mm to 100mm. The thickness of the layer influences the reaction rate, Fick's laws of diffusion may describe this interaction whereby the length of the diffusion pathway (i.e. layer thickness) is inversely proportional to the rate of reaction. This will therefore affect the overall efficacy of the technology and experimental data will need to be collected to define this relationship to aid the development of this technology. Moreover, study of the kinetics of the reaction of lime at 'low temperatures' (60- 90°C) indicate that the reaction rate and extent are dependent on humidity and can be impeded by the carbonate product layer which forms on the surface of CaO particles[18]. There are several other parameters which can affect the rate and extent of the ambient carbonation of lime, Table 1 highlights these.

Table 1. A summary of parameters affecting ambient carbonation of lime and the practical considerations that may need to be explored when using this reaction for a CDR technology.

Parameters	Reaction influence	Logistic consideration	Data collected?
Particle size	A smaller particle size increases the surface area, and increases the reaction rate if it were controlled by surface processes	Particles which are too small create dust issues when designing a process	[13]
Humidity	Higher humidity = increased rates. This reaction influence is well documented but the mechanisms behind why this occurs remain elusive[20]	How to maintain high humidity on a large scale/selection of locations with the right humidity.	[11,12, 18, 19]
Mixing	Mixing may increase rates and extents due to disturbing the product layer on the surface of the lime which can act as a diffusion barrier. Mixing can also increase exposure of unreacted lime to CO_2	Type of mixing such as mixing with an agitator, bursts of air or a rotating drum to name a few examples. Mixing frequency Energy requirements of mixing	No published data for lime
Layer thickness	Thinner layers reduce the diffusion length resulting in more lime exposed to high partial pressures of CO_2.	Thinner layers means that more land area will be required for an amount of lime. An optimum thickness will need to be determined which will require minimum land area for minimal compromise on reaction rate.	No published data for lime
Concentration of CO_2	A higher concentration of CO_2 may increase reaction rates and extents due to a greater availability of CO_2 to react, and mass transfer reactions are driven by partial pressure differences.	Most sources of atmospheric CO_2 are 0.04% CO_2 by volume. However, there may be the option to increase the CO_2 concentration by deriving the CO_2 from decaying organic matter. The source of CO_2 is ultimately from the atmosphere but has been concentrated through photosynthesis.	Some indications from the carbonation of products such as hempcrete which combines hemp and lime to form building blocks.[21] Aono[20] showed that higher concentrations of CO_2 increased reaction rates and extents. Conversely, other studies suggest that CO_2 concentration is independent of the overall reaction rate at low temperatures[18, 13]

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Parameters	Reaction influence	Logistic consideration	Data collected?
Air flow	Greater air flow exposes the lime to more CO_2 If performed as a fluidised bed it may also abrade the product layer on the surface of the particles to expose fresh lime to air = increased carbonation	The energy required for faster air flow may incur larger energy penalties and mean more CO_2 is emitted than is absorbed. Lime particles are usually of a small size so can be entrained at low air flow speeds which could cause a dust issue.	No published data for lime
Heap permeability	More permeable = more diffusion of air (for a given pressure gradient) and therefore increased carbonation	Heap permeability may change over the course of the carbonation reaction as the product layer builds on the surface. The permeability is also affected by particle size and shape, and gas flow.	No published data for lime
Temperature	Lower temperature may increase carbonation due to higher gas dissolution at lower temperatures	Controlling the temperature may be energy intensive, a consideration of the climate that the technology is applied will need to be considered.	[22]

To speed up the ambient carbonation of lime the fundamentals of the reaction must first be understood. Table 1 indicates that the reaction of CaO with CO_2 in ambient conditions is lacking in experimental data, understanding of mechanisms and exploration into how the different parameters may interact with one another.

Furthermore, data that has been collected is often contradictory further emphasising the need for robust data collection which considers the effects that each parameter has on the others[23].

THE LIME MARKET AND ITS FUTURE IN CDR

The current lime market size is estimated to be 41.93 billion USD producing 420 million metric tonnes in 2020 (Fortune Business insights, 2021) the growth of this market has been estimated under different he Intergovernmental Panel on Climate Change' (IPCC) emission scenarios which can be seen in Figure 1 below.

Production of lime has been estimated to rise to ~600 million tonnes by 2050 due to rise in demand from a growing population[25]. This lime is used in various applications such as in the iron and steel industry, construction materials and water purification[26]. Most of the emissions from lime production are from process emissions (calcination) (68%) and from fuel combustion (30%) with other processes such as mining and hydration of lime emitting comparatively less[27]. It is therefore important that lime be produced in a way that captures the process emissions and finds alternative methods and fuels for heating the kilns. The European Lime Association (EuLA) has suggested a pathway for the industry to reach net-zero emissions by 2050, it would therefore be essential to create lime without releasing CO_2. For example, using an oxy-fuel fired kiln coupled with carbon capture and storage[28], others have suggested solar kilns[29]. Low CO_2 lime production methods are still in early stages of development however the first UK based pilot plant for lime production in this manner has been built[30].

Figure 1. Estimated growth of production of lime under different emission pathways. [Information sourced from 25].
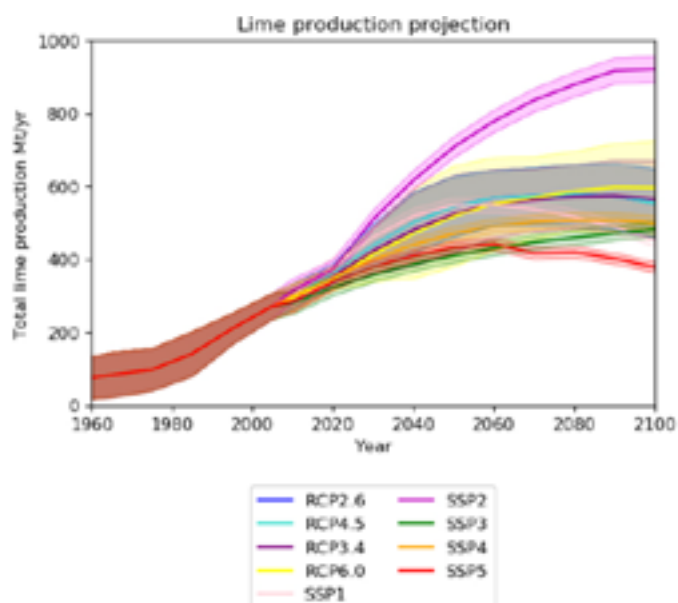
Reacting lime with atmospheric CO_2 could create a new CDR market for the CaO industry, helping them reach their own net-zero targets and possibly offer removal services for other sectors also. CaO reacts with CO_2 to form carbonates in a ratio of 1:0.78 respectively, this assumes 100% carbonation efficiency (i.e. 100% of the CaO will carbonate), although, experiments have demonstrated a 60-80% carbonation efficiency[11]. If ambient carbonation of CaO were to contribute 1 Gt per year goal, then this would mean that the production of CaO would need to increase by over 5 times its current size ('similar in size to the cement industry which grew from ~0.5Gt in the 1950's to over 4Gt of material production at present day'[25]). CaO which is bought and used in the current markets is around $100 per tonne, if bought for the purpose of CDR technologies buyers may be willing to pay more due to being able to sell carbon credits which are estimated to reach around £50/tCO_2e, (although this price is highly variable). Although there have

been no technoeconomic assessments done surrounding the use of CaO in CDR technologies and its effects on the CaO industry there has been an assessment of how the cement industry may be impacted by entering the CDR market using CO_2 mineralisation processes. The finding of this study suggests that with the additional revenue from the European emission trading scheme price leads to an additional profit of around £25 per tonne of cement sold[31]. This may suggest that if the CaO industry entered the CDR market lime could be sold at around $125 per tonne however a technoeconomic assessment would be needed to accurately assess this. Figure 2 below provides a range of potential values for the additional revenue which could be made by the lime industry under different emission reduction and carbon price scenarios.

Figure 2. Potential additional revenue for the lime industry under different emission intensity reductions across different carbon removal prices. Current emissions value used here was 1.5t of CO_2 per tonne of lime and removal potential of lime uses stoichiometric value of 0.78t of CO_2 removed by 1t of lime. [Projected cost of DAC at gigatonne scale from 32].
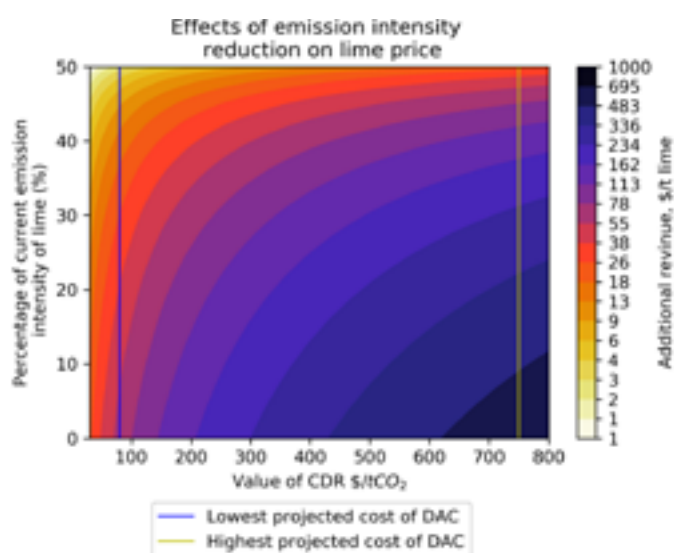

Figure 2 indicates that reduction will need to be over >60% for the additional revenue to be made at reasonable CDR values of $50-100 per tonne of CO_2 removed. At 52% of the current emission intensity of lime, CDR technologies using lime would only remove the CO_2 emitted in the process leading to no net removal and therefore no additional revenue.

The EuLA estimates that the equivalent of 33% of process emissions are removed from the air via passive/ambient carbonation of the CaO within its lifetime[33]. The application of the CaO has a fundamental role in the carbonation rate and extent for example in water purification carbonation is instantaneous, however, if the case of concrete used in the foundation of buildings carbonation is prohibited by the lack of exposure to air. The varied applications and the current chemical analysis methods of assessing carbonation rates and extents make estimating the current sequestration potential of lime products a difficult task leading to uncertain estimates. Moreover, the timeframe in which the emissions are removed was assessed up to 100 years, it's estimated that after 1 year 51% of the industry's CaO reaches a carbonation extent of 19.5%[26], this estimate highlights that CaO would need to be produced for the sole purpose of CDR if CO_2 is to be removed from the atmosphere on a scale and timeframe suitable

for climate change mitigation. The quantity of CDR CaO that would need to be produced could be reduced by recycling carbonated CaO as a feedstock to produce fresh CaO. This could be done via a looping system whereby the carbonated lime is collected and re-calcined to produce fresh lime which can then be used again, avoiding the extraction of limestone[11]. However, sintering, disintegration of the lime, or loss to the wider environment, may limit this.

FUTURE WORK

The current understanding of ambient carbonation of lime gives wide estimation values of rates and extents which makes scaling up this process as a CDR technology difficult. It is therefore important that fundamental rate and extent data be collected. Additionally, a suite of bench scale reactions and larger pilot scale experiments will be required before this technology can be safely scaled up. Furthermore, it is likely that the process will need to be designed in a way which uses minimal energy to remain net-zero, it will be necessary to use the chemical and experimental data to perform life cycle assessments to ensure the scalability of this technology.

CONCLUSION

Ambient carbonation of lime is a process that directly removes CO_2 from the atmosphere, however the logistics of using this reaction in a scaled-up CDR technology are not yet well understood. There are two main aspects of this technology where research must be focused, one is the production of zero carbon lime and the other is the method of carbonating this lime in ambient conditions with minimal energy inputs.

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Extracting Minerals . . . Manufacturing Products . . . Supplying Markets

Lime From Biogenic Calcium Carbonate for the Production of Slag-Based Alkali Activated Binder

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1 BACKGROUND AND INTRODUCTION

Concrete is one of the most extensively used materials for construction with almost three tonnes used annually for each person on Earth[1], making it the second most consumed substance on the planet after water. The most common binder for the production of concrete is Ordinary Portland Cement (OPC), which contributes a total of 5-7% of the global man-made carbon dioxide emission from fuel combustion and thermal decomposition of limestone[2]. If the concrete industry was a country, it would be the third highest emitter in the world.

A possible solution to curb the carbon emission of concrete production without losing the desired properties of concrete such as strength and durability is to substitute the clinker with other, less energy intensive binders.

Alkali-activated binders (AAB) are considered high-potential alternative materials for Portland cement substitution under certain conditions. The technology exploits the reaction between silicoaluminate materials (called precursors) and alkali chemicals (called activators) to produce a solid, dense binding matrix[3]. Precursors can be sourced among waste/by-product streams to produce concrete with good mechanical properties and good durability against physical and chemical attacks. However, their utilisation is still hindered by the relatively high cost of the alkali chemicals required for the reaction and their environmental impact, among other factors[4]. Commonly used chemical alkaline activators includes sodium-based activators for the increase of pH (such as sodium hydroxide) and/or the availability of ready-to-react silicates (such as sodium silicate). However, practical problems in handling high pH solutions, rapid setting time, as well as high production cost[5] are encountered in the engineering practice.

Other chemical activators that may provide the desired alkali chemical environment are calcium oxide (CaO) and calcium hydroxide ($Ca(OH)_2$), whose conventional sources rely from the calcination of limestone ($CaCO_3$) and have been investigated as promising activators for slag – ground granulated blast furnace slag (GGBS) in literature.

While significant effort has been spent on investigating the effect of commercially available chemical activators for GGBS, more information is needed about the use of alternative activators. Research worldwide have been investigating the production of alternative activators obtained with low-energy processes or sourced from waste or by-product streams, which can increase the sustainability, solve the high-cost problem of chemical activators, as well as reduce the global waste problem.

Alternative sources of calcium carbonate from renewable sources such as eggshell and seashell have been investigated mainly to be used as fillers in concrete, but not much attention has been given to the use of waste bio-derived calcium oxide or hydroxide for the activation of alkali activated binders. This paper discusses the preliminary results obtained from oyster shell and eggshell as a source of lime for the GGBS activation in alkali activated binder.

2 LITERATURE REVIEW

2.1 Ordinary Portland Cement (OPC)

As the second most consumed substance in the world, the production of concrete is responsible for 5%-7% of the total man-made CO_2 emission[6]. The production process includes combining and heating natural resources such as limestone and clay in a kiln to a temperature as high as 1400°C to produce the clinker, which is then ground and blended with some gypsum in a ball mill. The combined effect of burning fossil fuels to reach the high temperature needed for the thermal decomposition of limestone ($CaCO_3$)[7] and the direct emission of CO_2 due to the de-carbonation of limestone, results in a CO_2 emission of 0.8 – 1 tonne for each tonne of OPC produced. Naik[7] stated that the requirements for sustainable alternatives are low energy usage, minimal waste production, abundance of resources availability, and high-performance finished product, among others. A competitive or possibly lower cost of the sustainable alternative are also sought to be viable for the industry.

2.2 Supplementary Cementitious Material

One of the solution currently adopted to reduce the large carbon footprint of concrete production is to substitute a certain percentage of OPC in a concrete mix with supplementary cementitious materials (SCMs) sourced from commercial or industrial by-products. Among the advantages of adding or substituting SCMs to a concrete mix are increased strength, reduced cost, reduced carbon emission, and reduced permeability[8]. Numerous studies have observed the effect of substituting percentages of OPC to different kinds of SCMs.

2.2.1 Industrial By-products

Yang et al.[9] investigated the effectiveness of fly ash, GGBS, and silica fume substitution on the reduction of CO_2 emission from OPC production and concluded that the CO_2 emission decreased distinctly as 15-20% of OPC is substituted with SCMs. On the other hand, Samad and Shah[10] reviewed the strength of concrete made using partial substitution of OPC with GGBS, fly ash, and rice husk ash and concluded that, although the strength gain is slower in concrete mix with GGBS, blended mixes are stronger than neat OPC-based concrete in the long term. The review also recommends 50% as the maximum GGBS substitution in the concrete mix and a curing temperature of 20°C. It is to be noted that the maximum allowable substitution of slag according to BS-EN 197[11] for CEM III/C Blast furnace Cement is 95%.

2.2.2 Other Waste

Several studies on partial replacement of OPC using different waste material are available in the literature. Yerramala[12] investigated the use of poultry waste by substituting different percentages (5-15%) of eggshell ash in OPC concrete and concluded that a 5% eggshell ash replacement is optimum since it achieved higher strength at 7 and 28 day of age compared to the control concrete.

Recycled agri-business wastes such as eggshell ash and rice husk ash have been investigated by Asman et al.[13] to identify the optimum percentage of their use as OPC replacement. The research suggested that a strength reduction is to be expected when some OPC is replaced by eggshell ash, therefore a pozzolanic admixture such as rice husk ash needs to be added to ensure a suitable strength of the concrete. The study concluded that concrete made using 6% eggshell ash and 4% rice husk replacement have compressive strength 24 MPa higher than neat OPC-based concrete having strength of 18 MPa at 28 days. In general, the literature suggests that the highest percentage of OPC replacement using waste materials should not exceed 10-15%, in order to mitigate possible strength decreases.

2.3 Alkali Activated Material

A more radical solution to significantly reduce the emissions of concrete production is to completely remove OPC from the mix. Alternative, non-clinker-based binder has to be used to cast a product with suitable properties. As observed by Provis and Deventer[14], the concept of alkali activated materials to substitute OPC was patented by Kühl, a German cement chemist and engineer, back in 1908. Alkali activated binders are produced by mixing Si, Al and Ca donors (precursors) with alkaline activators[15].

2.3.1 Precursors

Materials with either high silica and alumina or high calcium have been investigated extensively as ideal cementitious component in an alkali activation [3, 16]. Most common precursors are highly amorphous GGBS, metakaolin or fly ash. Haha et al.[17] observed that when using adequate activators, GGBS is able to achieve high strength development along with rapid setting time, high durability, and high resistance to chemical attacks.

2.3.2 Alkaline Activators

Yang et al.[9] commented that "strong alkalis such as alkali hydroxide (ROH) and silicic salts of R2O(n)SiO2 where R indicates alkali metal ion such as Na, K, or Li" are effective in increasing the hydration reaction of GGBS. Purdon[18] experimented 30 different GGBS and activators and concluded that potential problems in this method of construction include high sensitivity from water added to the mix and practical difficulties in handling concentrated caustic solutions. These problems are recurrent with commonly used activators such as sodium silicate (Na2SiO3) and sodium hydroxide (NaOH). Rapid setting time, relatively high cost, and high risk due to the high pH value of sodium hydroxide triggered the need for safer and more affordable activators.

Kim et al.[5] investigated the use of calcium hydroxide (Ca(OH)$_2$) and calcium oxide (CaO) as activators for GGBS and concluded that the paste made using calcium oxide developed a higher mechanical strength (42 MPa) compared to the one activated using Ca(OH)$_2$ (23 MPa). The amount of activator used in the study was 6.25% of the total mix weight and the water to cement ratio was set to 0.4. Jeong et al.[19] investigated a CaO-activated slag system using 10% wt of activator and 40% wt of water, obtaining materials with satisfactory mechanical properties.

2.3.3 Waste-based Activators

Although alkali activated material have the potential to increase the sustainability of concrete production, the use of commercially available chemical activators has negative environmental impacts. The use of waste-based activators for the production of alkali activated material seems therefore a promising solution to this problem. Numerous studies investigated the effect of partially substituting commercial

waste materials such as rice husk ash and eggshell powder[13] to cement mixes, but only few have investigated the calcination of waste materials for their use as activators of GGBS. Gu et al.[20] studied the activation of GGBS using calcined natural dolomites, however, no example of use of biogenic lime is available in the literature.

2.4 Use of biogenic lime

Conventional CaO is obtained by calcining limestone, which is 97-98% composed of calcium carbonate in the form of the mineral calcite[21]. Biogenic materials that have similar composition as limestone includes eggshell and oyster shell, which usually end up in landfills and have no other use currently. In a survey done by Egg Info[22], a total of 13,158 million eggs were consumed in the UK in 2018. By assuming an average eggshell mass of 6-7 gr[23], a total of 78,000 tonnes of eggshell each year would be available in the UK. According to Yerramala[12], eggshell waste utilisation is limited to plant fertilizer and animal feed, but most of it ends up being a major problem in landfills in urban areas.

There has been a lot of interest around the possible usage and application of eggshell waste recently, with notable studies conducted by Baláž et al.[24] that investigated the potential use of eggshell waste in catalysis a well as other pharmaceutical uses, and by Ahmed et al.[25] which summarised the various biotechnological applications of eggshell waste such as wastewater purifiers, and its potential in replacing limestone in steel and paper manufacturing amongst others.

Recent projects have been investigating the use of biogenic lime for engineering applications, such as:

- Dr Ana Heitor (University of Leeds) is currently investigating the feasibility of the use of lime sourced from calcium carbonate waste (from industrial food waste sources such as eggshells and seashells) as a soil stabiliser.

- The project "Advanced Materials using Biogenic Calcium Carbonate from Seashell Wastes" (CASEAWA) aims at producing chemically and physically functionalized biogenic calcium carbonate particles (FbCCP) using fishery industry waste seashells from mussels and oysters[26]. The UK consumes around 1100 tonnes of oysters per annum[27], with shellfish disposal costs exceeding £60 per tonne.

- The European project LIFE EGGSHELLENCE, intends to develop a prototype aimed at obtaining calcium carbonate from eggshell (Bio-CaCO$_3$) for its subsequent use in the manufacturing of ceramic wall tiles.

- The FP7 EU project SHELLBRANE (Separating eggshell and its membrane to turn eggshell waste into valuable source materials) developed a prototype able to process 60 kg/h of eggshell waste producing both membrane and mineral shell with a high degree of quality.

3 METHODOLOGY AND THEORY

3.1 Methodology

Oyster shell powder was chosen as the biogenic carbonate to be calcined and investigated for its efficiency to activate GGBS. Oyster shell powder was examined using XRD test to identify the percentage of calcium carbonate present before calcination.

Thermal decomposition temperature and process duration for each material were investigated with TGA tests. Weight reduction percentage and XRD test on calcined materials were carried out after the

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calcination process to observe the percentage of calcium oxide present and to examine whether the calcination process was completed.

The calcined oyster powder was then mixed with GGBS, sand, and water to produce a mortar that was tested in compression at 1, 7, and 28 days of age. Eggshell powder was also characterised in order to be compared with oyster shell powder.

3.2 Theory
3.2.1 Activation of Ground Granulated Blast furnace Slag (GGBS)
GGBS is formed by cooling molten slag with water and grinding it to produce a glassy granular material that consists of mainly of SiO_2, CaO, MgO, and Al_2O_3. The short-term compressive strength of concrete made using GGBS is usually lower than that of OPC concrete, thus there is the need either to increase the fineness of the GGBS particles, apply thermal cycles to increase the curing temperature, or use chemical activators to enhance its reactivity[28].
Further hydration in GGBS needs a chemical activator because within contact with water, an impermeable coating of aluminosilicate forms on the surfaces of GGBS grains[29]. A high-pH activator is then needed to polymerize the GGBS that will result in the forming of calcium aluminosilicate gel that hardens over time[30].

3.2.2 Calcination Process
Calcination reaction takes place when a carbonate material is heated to or above its thermal decomposition temperature. The calcination process for the decomposition of calcium carbonate ($CaCO_3$) typically begins when the temperature is between $780 - 1340°C$ and the temperature must be maintained after the reaction starts[31]. The chemical reaction is:

$$CaCO_3 \longrightarrow CaO + CO_2(s)$$
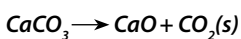
When calcium oxide (CaO) is mixed with water, it produces a high-pH compound which is calcium hydroxide ($Ca(OH)_2$) according to the following reaction:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$
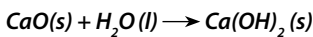
3.2.3 Activator's Degree of Purity
Calcium oxide (CaO) activators made using the calcination of calcium carbonate ($CaCO_3$) might not consist of pure CaO. This might be due to the incomplete calcination process or to impurities in the material. Some impurities as stated by Lewis[32] includes calcium carbonate ($CaCO_3$), magnesium (Mg), iron (Fe), and aluminium oxide (Al2O3). Knowing the degree of purity of activators used in alkali activated material is important for achieving the desired activator dosage in each mix tested. The purity of activators made from calcining waste material were assessed using X-Ray Diffraction (XRD) test.

4 EXPERIMENTAL WORK

4.1 Materials
GGBS was supplied by ECOCEM[33], and it was ground and dried in a plant in Ireland. The Al_2O_3 content of the product is guaranteed to be less than 14% and the rate of vitrification ensures that the glassy content (amorphous phase) is higher than 95%.

Commercially available crushed oyster shell (poultry feed addition to improve the egg production) was bought from Wilko[34].

Eggshell powder was sourced independently from British free-range eggs which was later washed and oven dried to a temperature of 180°C for 30 minutes.

Dry silica sand and tap water were used for the mortar mix with a water-to-solid ratio of 0.4.

4.2 Experimental Procedures
4.2.1 Manufacturing of Activator
Crushed oyster shell was first ground using RETSCH PM100 Planetary Mill with agate balls to produce a finer powder, which was tested for its mineralogical composition using Bruker D8 ADVANCE X-Ray Diffractometer with Cu-Kα radiation of λ=1.5418 Å, with scanning speed equal to 0.017°/s at 40 kV and 40 mA in the 2-theta range 5°- 60°.

Thermal Gravimetric Analysis (TGA) tests on oyster shell powder and eggshell powder were carried out by placing the powdered samples in a 70 μm pan and measuring the mass at room temperature. A Mettler Toledo TGA/DSC 1 with a N2 rate of 50ml/min, temperature range of 25-950°C and a heating rate of 10°C/min was used. After completion of the test, the weight of the sample was recorded to evaluate the weight reduction percentage. A second test was carried out with heating rate of 50°C/min to rapidly reach the thermal decomposition temperature of the material, which was then maintained constant for 3 hours to understand the kinetics of the calcination process.

The calcination of oyster shell powder was carried out with a Carbolite CWF1200 furnace. The furnace was started at 25°C and heated until it reached the temperature of 875°C. The calcination temperature was then maintained constant for around 3 hours. When cooled, the weight of the calcined oyster shell powder was recorded and the calcined powder kept in an airtight container in order to prevent any contact with air moisture.

Chemical composition of the calcined oyster powder was carried out using TESCAN VEGA3 Scanning Electron Microscope (SEM) equipped with Oxford Instrument X-MAXN Energy Dispersive Spectrometer (EDS).

4.2.2 Mixing of Mortar
The GGBS was activated using the calcined oyster shell powder. Three different percentages of activator (5%, 10%, and 15% wt%) were added to 500g of GGBS. Sand-to-binder ratio was fixed at 2.75, whereas water-to-solid ratio was kept at 0.58, as the initially selected 0.4 ratio led to low workability of the mix. The proportion of each tested mixture can be seen in Table 1. The quantities of calcined oyster powder added in the mix were determined by assuming an average efficiency of the calcination process equal to 50% (see section 5.1.2).

Table 1. Mix Proportions of the Tested Samples

Mix Label	GGBS (g)	wt % of activator (%)	Calcined Oyster Powder (g)	Water (ml)	Sand (g)
A	500	5	50	290	1375
B	500	10	100	290	1375
C	500	15	150	290	1375

The GGBS, calcined oyster shell powder, and sand were dry-mixed in a Quattro MXP004 Planetary Mixer for 3 minutes before water was added. The mortar was mixed for an additional 5 minutes before being cast in

six 5cm cubic PVC moulds. The moulds were vibrated using Controls Electromagnetic Sieve Shaker 15-D0407/B for one minute to eliminate air bubbles. The moulds were then wrapped in cling film to prevent rapid loss of moisture during curing. The cast mortar was left at room temperature for 24 hours before demoulding and cured further in the same condition until tested.

4.2.3   Compressive Strength Test
Compressive strength test of two cubes for each mix was planned at 1, 7, and 28 days of curing. However, as the 1-day strength was found to be extremely low, the testing plan was modified allocating three cubes for the 28 day tests. A Controls Compression Test press Model 50-C4600 and Controls Model 50-C1201/B were used to determine the compressive strength of mortars. The applied loading rate was 250 N/s.

5   RESULTS AND DISCUSSION
5.1   X-Ray Diffraction (XRD) Test Results
5.1.1   Oyster Shell Powder
The XRD result for oyster shell powder is shown in Figure 1. The mineralogical composition from semi-quantitative analysis on the main peaks suggested that the oyster powder sample consists of about 35% Calcite and 65% Aragonite (polymorphs of calcium carbonate). A reasonable assumption that oyster shell powder is a pure crystalline material is made based on the flat baseline of the graph. This result confirmed the outcomes of a study on biogenic and non-biogenic calcium carbonates by Boaz et al.[35], which concluded that mollusc shells are primarily composed by two polymorphs of calcium carbonate: calcite and aragonite along with small percentages (0.1-5 wt%) of organic molecules. The test confirmed that oyster shell powder is mainly composed of calcium carbonates and therefore it is a suitable candidate for calcination and use as GGBS activator.

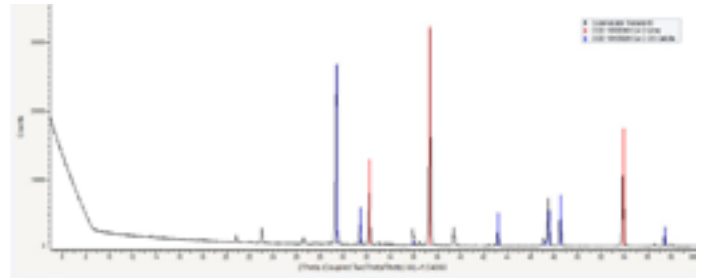**Figure 1. XRD Test Result for Oyster Shell Powder**
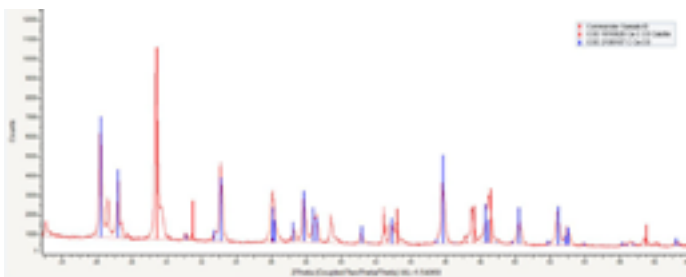
5.1.2   Calcined Oyster Shell Powder
The XRD result for the calcined oyster shell powder is shown in Figure 2. XRD diffractograms and data from the weight recorded before (422.02 g) and after calcination (307.5 g) suggested that the calcination process was incomplete, achieving only 27% of weight reduction. Soisuwan et al.[36] stated that weight loss from calcination should be in the range of 40-50%. The XRD semi-quantitative analysis detected only a 45.5% percentage of CaO in the sample, confirming that the calcination process was not completed and that 54.5% of the sample was still in the form of calcium carbonate ($CaCO_3$).

This leads to the assumption that the efficiency of the activator as evaluated from its degree of purity was roughly 50%. The incomplete decomposition might be caused by coarse particles that; did not properly calcine, or, re-carbonated after contact with air, or, needed a longer oven processing time to complete their reaction. It was also observed that calcined oyster powder seemed to agglomerate in particles bigger than the pre-calcination size.

Figure 2. XRD Test Result for Calcined Oyster Shell Powder (red lines: CaO; blue lines: $CaCO_3$)

5.2   Thermo-Gravimetric Analysis (TGA) Test Results
5.2.1   Oyster Shell Powder
The results of TGA on oyster shell powder are shown in Figure 3. Derivative Thermo-Gravimetry (DTG) curve allowed to appreciate variation of mass losses in better details. Mass loss of the sample tested was 43.45%, indicating that the complete calcination was achieved. The thermal decomposition of oyster shell powder appeared to start around 600℃ and was completed by the time the temperature reached 825℃ as shown from the highest rate of change in the DTG. Therefore, it was concluded that 825℃ can be considered the target temperature for calcination, with an additional 50℃ margin of safety, to ensure complete calcination.

In order to check if the kinetic of calcination was influenced by the time duration of the heating process, a second test was carried out with a sharp temperature increase (rate 50 ℃/min) followed by a constant temperature plateau. It was observed that the mass loss was completed as soon as the temperature reached 875℃, and no further changes were recorded thereafter. It could therefore be concluded that the calcination did not seem to be influenced by the firing time. However, it must be clarified that this observation was relevant only to the TGA testing conditions, applied on a few milligrams of sample. As the amount of material, its grain size and the effectiveness of thermal transfer in an oven can play a role in the thermal decomposition, it was decided to keep the powder in the oven for three hours, leaving enough time for the reaction to be completed.

5.2.2   Eggshell Powder
In order to check any differences between the thermal decomposition kinetics of oyster shell and eggshell respectively, TGA tests were carried out also on a sample of eggshell. The thermal decomposition of eggshell was observed to start slowly when the temperature reaches 300℃, gradually losing around 2% mass before it intensifies at around 600℃. Similar to oyster shell powder, the thermal decomposition of eggshell powder most likely ended at 800℃ according to the DTG plot. A comparison of the percentage mass retained of oyster shell powder and eggshell powder is shown in Figure 4, where both appear to have a very similar thermal decomposition temperature and rate.

5.3   Scanning Electron Microscope (SEM) Test Result
The morphology and chemical composition of the calcined oyster shell powder was observed using a SEM equipped with Energy Dispersive Spectrometer (EDS). Two spectra chosen from the sample were evaluated and the weight percentage of chemical elements for each spectrum obtained as shown in Figure 5. The first spectrum was observed to have a high total weight percentage of calcium and oxygen of 95.3%, which can suggest that the particle was fully calcined. The second spectrum only had a total of 75% weight percentage of both calcium and oxygen, an indication of incomplete calcination.

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The SEM image taken reveals that the calcined oyster powder has a large range of particle size distribution as seen in Figure 5. This might be caused by the rapid heating rate of the furnace during the calcination process that will result in the decrease of surface area of the calcined product, which might reduce the hydration rate during mixing[37].

Figure 3. Oyster shell powder TGA test results. (a) Temperature profile (increase at constant rate), (b) TGA and DTG with constant temperature increase rate,(c) Temperature profile (rapid increase and plateau), (d) TGA and DTG with rapid temperature increase and plateau
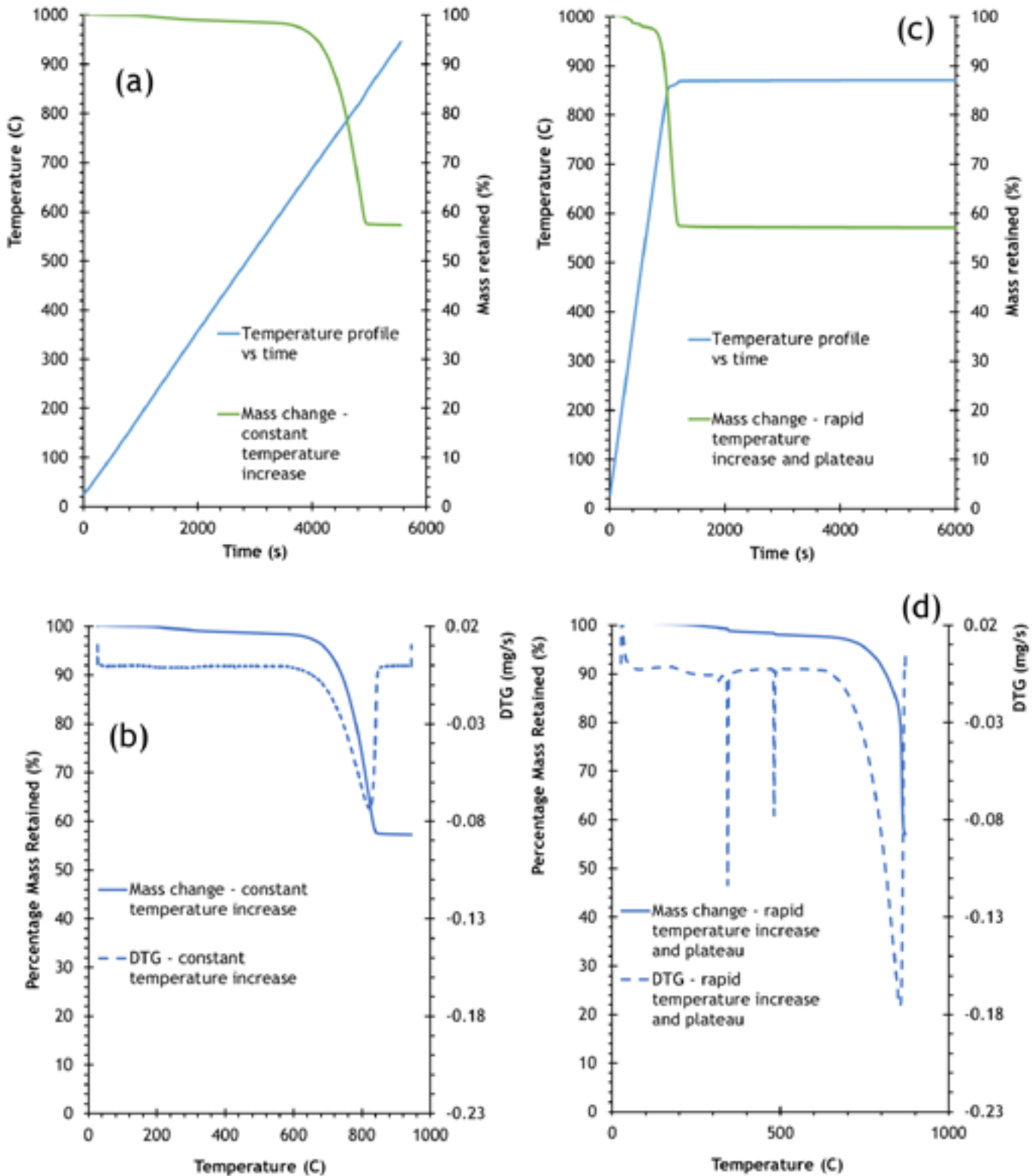
Figure 4. TGA on eggshell and oyster shell powders
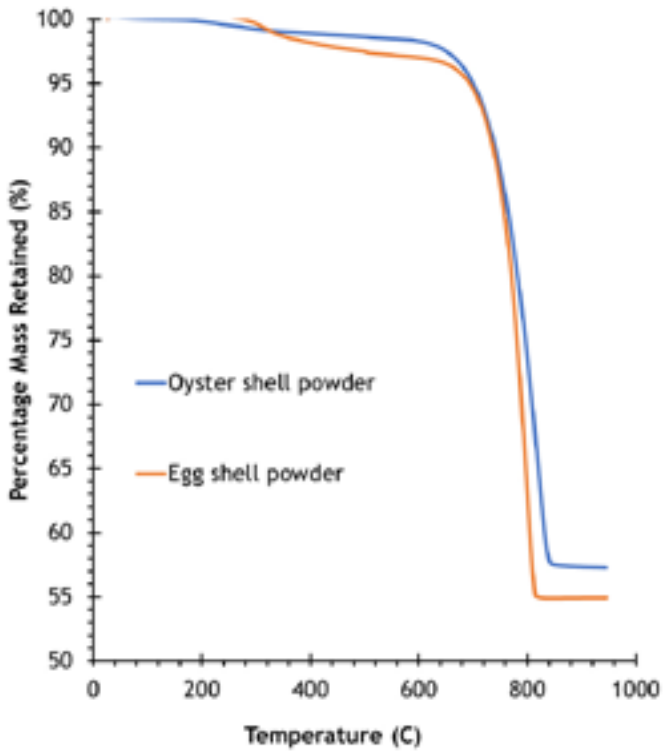
Figure 5. SEM/EDS analysis on calcined oyster shell powder

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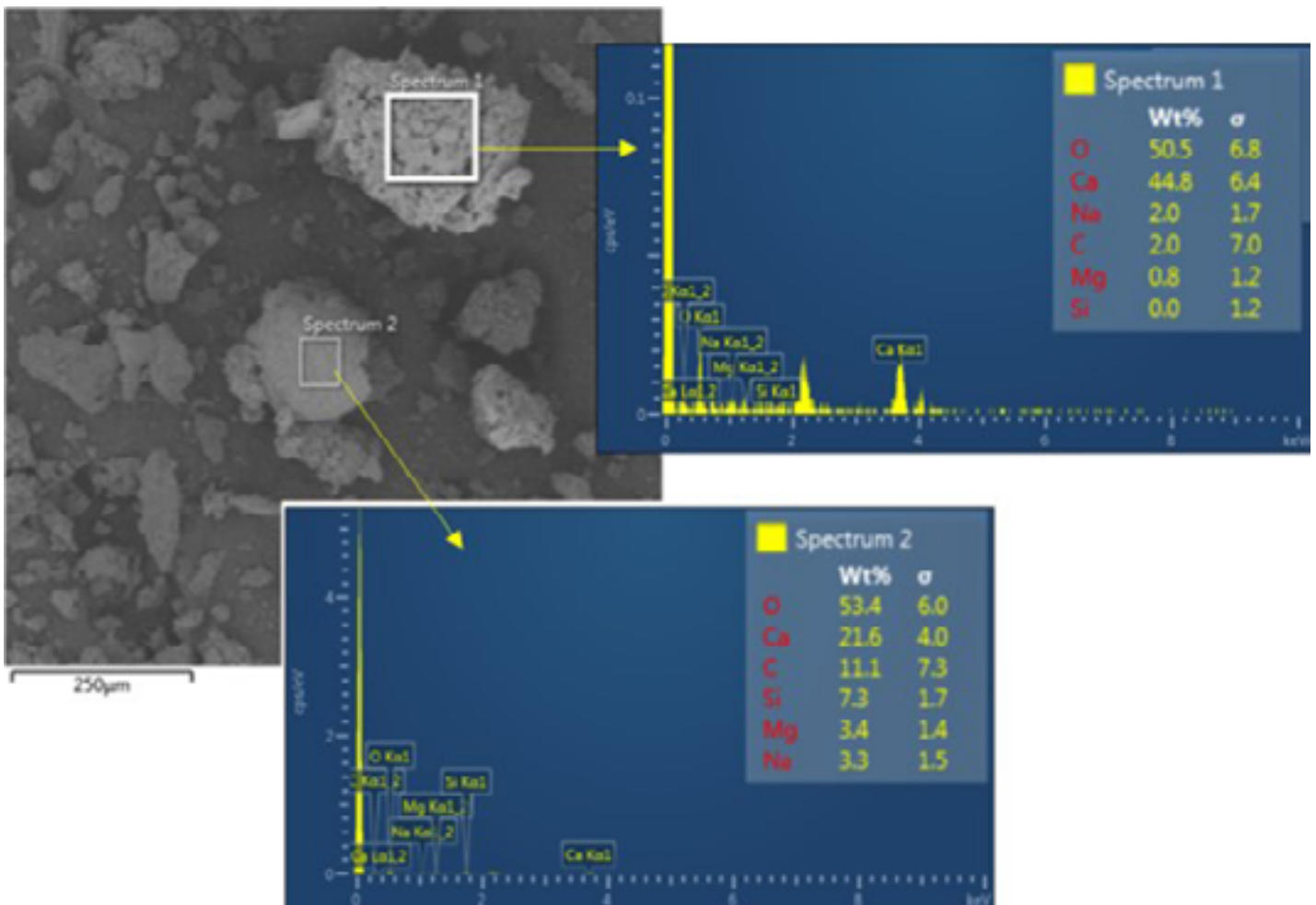
5.4 Compression Test Result

The average compressive strength test results at 1,7, and 28 days are shown in Figure 6. Considerably low compressive strength was measured at 1 day of age, with mix A showing half the strength given by mixes B and C. This soon changed as at 7 days all three mixes exhibited a very similar compressive strength in the range of 12-14 MPa, with the maximum strength obtained from mortar made using 15% of activator. The rate of strength gained from each mix from 7 to 28 days is less significant compared to 1 to 7 days, with the maximum strength gained by the mortar made using 10% of activator. Interestingly, the compressive strength gained by mixture B and C at 28 days is nearly identical, with a difference of only 0.06 MPa.

This was unexpected as the chosen amount of activator used was predicted to have more influence on the mortar compressive strength.

It was also observed that the cubes from all mixes tested at 28 days still had a slightly high moisture content as the inside of the cube was moist to the touch. This might indicate that there was a potential to further develop the compressive strength with longer curing time. The inside of the crushed cube showed a slightly green colour from the presence of iron sulfur (FeS) and manganese sulfur (MnS), see Figure 6[37]. Mortars also showed the presence of air bubbles creating voids, as can also be seen in Figure 6. This might have influenced the low compressive strength and would suggest that longer duration of vibration should be allowed.

Figure 6. Compressive Strength development of mortars (results in MPa)
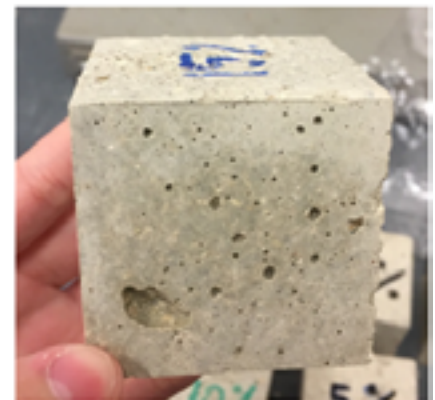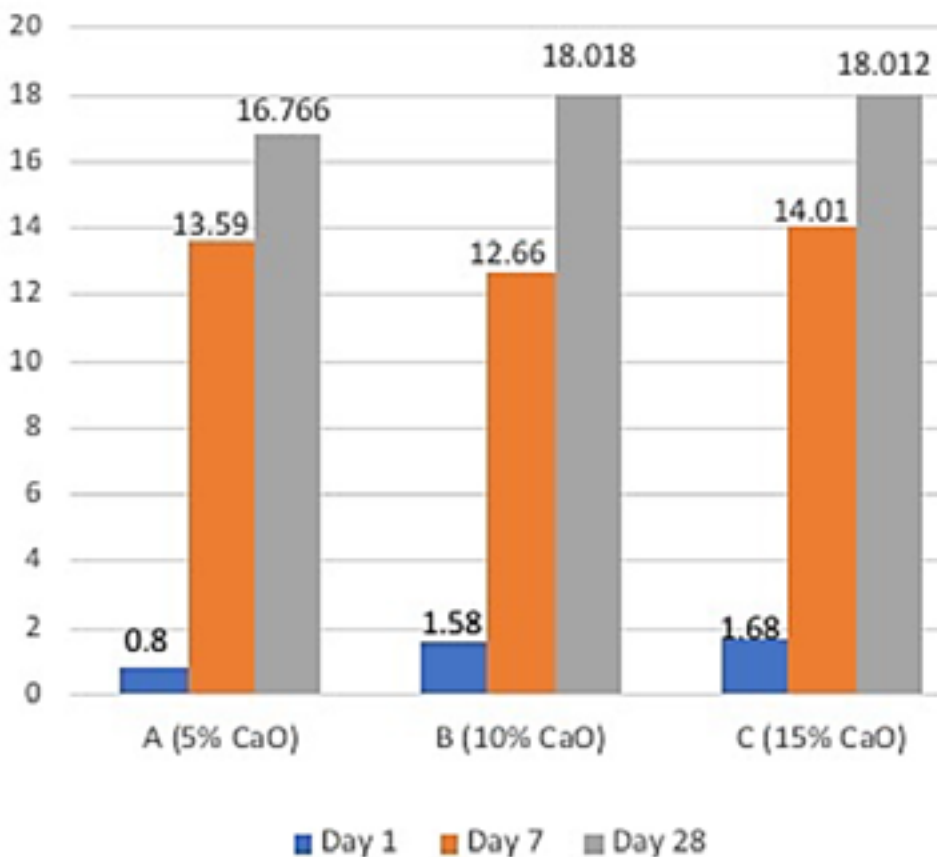
5.5   Discussion

The activation of GGBS using calcined biogenic calcium carbonates from oyster powder have been observed to be successful with a maximum mortar compressive strength of 18 MPa at 28 days of age using 10% wt of natural activator and 0.58 w/s ratio. This value is substantially lower than what Kim et al.[5] obtained by using 6.25% wt of chemical CaO activator and 0.4 w/s, which resulted in a maximum compressive strength of 42 MPa. Several possible reasons that can explain the difference between the results obtained in this study and the literature results can be listed.

As the strength of alkali activated GGBS is known to be highly influenced by the water content, increasing the mixing water mass to 0.58 might be one of the reasons behind the low compressive strength obtained. Water will dilute the hydroxide ions concentration, resulting in a lower pH value that in turns would reduce the effectiveness of the activator. Furthermore, the extra water could also result into the formation of voids that lower the density of the mortar and its strength. Another variable that can have impacted the strength development refers to the large particle size observed in the calcined oyster powder. Larger particles would lead to lower surface areas, which would in turns decrease the hydration rate in the mortar. This issue could be fixed by setting a lower heating rate during calcination, or by further milling of the calcined oyster powder before mixing.

The negligible differences in the compressive strength measured on the three mixes leaves doubts whether the activator dosage should be increased to deliver the optimum mortar compressive strength. Repeating the experiment using a wider range of different percentages of activator would be recommended in order to achieve a conclusive optimal dosage of biogenic lime for the activation of GGBS. Further research includes increasing the fineness of the activator to prevent excessive water addition during mixing so that a mortar with high workability can be made. Due to the high moisture content observed inside of the cubes even after 28 days, testing the cube after 56 days can be also recommended for checking the maturity rate of the mortars.

Optimisation of calcination process needs to be further analysed due to the incomplete calcination of oyster powder confirmed by XRD test and SEM-EDS. Potential approaches includes producing a more accurate estimation of the percentage of CaO in the calcined activator and ensuring even heat distribution during calcination.

Although eggshell and oyster shell powders were observed to have similar thermal decomposition temperature, it is essential to carry out a full material characterisation and assess the effectiveness of eggshell in activating GGBS. XRD can be used to detect the amount of calcium carbonate present and mortar made using different percentages of calcined eggshell powder can be produced to evaluate the effectiveness of the alternative waste-based activator.

6   CONCLUSIONS

This paper discusses the preliminary findings of a research aimed at delivering biogenic-derived lime for the activation of GGBS. Calcined oyster shell powder was chosen to be used as the biogenic activator, however, other biogenic carbonate sources such as eggshell powder could be considered.

Overall, calcium oxide made from the calcination of oyster shell powder with a temperature of 875℃ in 3 hours was observed to be a feasible GGBS activator. However, due to incomplete calcination confirmed by

XRD and SEM-EDS test, the effectiveness of the activator was estimated at about 50%. Although the production of the activator still needs a temperature of 875℃, it is significantly lower than the temperature of 1400℃ needed to produce OPC, therefore reducing both the cost and carbon dioxide emission of the production.

The compression test results on mortar cube samples manufactured using GGBS activated with calcined oyster shell suggested that mortar made using 10 wt% activator reached a strength of about 18 MPa after 28 days of age. As stated in literature review, not much research has been done to evaluate the effectiveness of waste based biogenic GGBS activator, and thus it is not easy to compare data on compressive strength.

Considering that the mortar was made using nearly all-waste material, the compressive strength achieved was considered successful, and confirmed the possibility of using biogenic-derived lime for the activation of GGBS. Optimisation of activator and investigations on cost of production and carbon dioxide emission of calcined biogenic carbonate activated GGBS would be the next recommended steps to ensure that it is an effective, sustainable, and viable alternative to OPC.

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Influence of Test Setup on Sulphate Swell Measurements

Using low and high sulphate soils to assess swell quantified by different test set ups

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ABSTRACT

Sulphate swell is a known risk in lime stabilisation and existing literature attributes this to water inundation causing growth of ettringite or thaumasite. Recent studies show sulphate swell is greater at UK site relevant temperatures of 10°C compared to the 20°C often used in laboratory tests and that a mould around samples could limit water ingress.

This study assessed the swell potential of a low and high sulphate soil treated with 3% quicklime. A range of different swell test set ups promoted environments potentially relevant to site scenarios. Two of the swell test methods were based around British Standard methods for soaked California Bearing Ratio (CBR) and accelerated swell tests but using 10°C soaking water and variations saturated with gypsum. A third novel set up (The Nottingham Trent University – NTU - sulphate swell test) permitted 10°C water to access specimens via a 1-2mm sand surround and including variations with aerated water intended to promote thaumasite growth.

Findings confirm the pathway for water access is highly influential in the degree of swell measured by tests at 10°C, with the most swell measured in the unconfined accelerated swell tests. Adding gypsum to the soaking water caused up to 6.5% expansion in low sulphate samples that otherwise did not swell in tap water, and even higher expansion (22%) in the high sulphate soils. Swell was much less in CBR tests with intermediate amounts in the NTU test. Mineralogy tests indicate only very small amounts of ettringite formed in any specimen and the sulphate swell appears due to unbound water and a potential swell mechanism is discussed.

INTRODUCTION

A common practice in earthworks for UK construction projects is the treatment of cohesive fill with quicklime. When quicklime is rotavated into cohesive soils, a series of reactions including exothermic drying, cation exchange and pozzolanic reaction occur to result in enhanced engineering properties of the compacted material[1].

The main benefits of using lime stabilisation as a ground improvement method are:

■ Improved engineering properties such as high strength, durability, and frost resistance.

■ Reduced waste by treating material already on site, rather than removing and importing new material which increases travel to and from site.

■ Allowing for wet ground to be dried in winter, therefore allowing earthworks activities to be carried out all year round.[3]

Although lime stabilisation brings significant benefits, substantial and damaging swell (sulphate swell) has been associated with treatment of sulphate bearing soils, e.g. from gypsum or pyrite[1]

BACKGROUND

Sulphate Swell

Sulphate swell is heaving of the treated layers following inundation with water which when sustained can lead to damage of the structures above. Although reports of damage from sulphate swell are relatively rare, when they do occur the additional time and cost to construction projects can be substantial. This form of swell in lime treated layers is associated with the growth of expansive minerals such as ettringite and thaumasite[4]. The chemistry behind this sulphate swell process is summarised further below but in general, swell appears worse under specific environmental conditions e.g. low temperatures and increased water availability[1].

Sources of Sulphate

Primary sources of sulphate are found as sulphate salts such as gypsum, which is the most common. In its pure state, gypsum is semi-soluble in water however, its solubility can be four times higher when in the presence of other minerals such as halite ($NaCl$)[5]. While gypsum has relatively low solubility, fluctuating groundwater to flood the lime treated layer would allow for continuous dissolution of gypsum and growth of new minerals (e.g. ettringite). Hence, an environment which replenishes sulphate ions available for reaction is created.

Secondary sources of sulphate come as a by-product of chemical reactions such as oxidation. The mineral Pyrite (FeS_2) is a common sulphide that is present in soils and when both air and water are available, it oxidises to form sulphuric acid. Where calcium carbonate is also present, a buffering reaction neutralises the sulphuric acid and gypsum is formed as a by-product. Pyrite oxidation to gypsum alone results in at least 35% expansion of the original volume[6] and the resultant gypsum becomes available to form ettringite with further heave potential[7]. Floyd et al. (2003) suggested that environments of either oxygenated groundwater or atmospheric conditions are needed for significant pyrite oxidation prior to formation of ettringite[12]. Soil deposits considered higher risk of sulphate swell often contain a combination of primary and secondary sulphates which should be identified during pre-contract laboratory testing, by determination of a total potential sulphate (TPS) value of the soil[8]. A soil TPS of <0.25% is considered minimal swell risk, 0.25% -1% requiring close monitoring with swell tests and >1% of considerable concern[8]. However, specific working methods e.g. including ground granulated blast furnace slag with the lime binder may be used to successfully stabilise soils with TPS up to 2%[8].
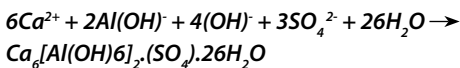
Ettringite and Thaumasite

Ettringite (eq.1) is an expansive mineral which may form from calcium, aluminate and sulphate in an alkaline environment. Ettringite is a hexacosahydrate and where the hydration water is drawn in from an external source a 137% volumetric expansion occurs[6]. Thaumasite has a similar mineralogical structure to ettringite and is described as
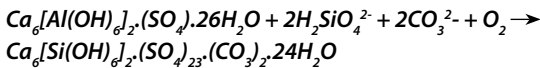
forming either via ettringite alteration (eq.2), or nucleation on the surface of existing ettringite[9]. Thaumasite growth direct from solution and without ettringite is considered to be extremely slow or unlikely[9].

Eq.1
$$6Ca^{2+} + 2Al(OH)^- + 4(OH)^- + 3SO_4^{2-} + 26H_2O \rightarrow Ca_6[Al(OH)6]_2.(SO_4).26H_2O$$

Calcium + Aluminium Hydroxide + Hydroxide + Sulphate + Water → Ettringite

Eq.2
$$Ca_6[Al(OH)_6]_2.(SO_4).26H_2O + 2H_2SiO_4^{2-} + 2CO_3^{2-} + O_2 \rightarrow Ca_6[Si(OH)_6]_2.(SO_4)_{23}.(CO_3)_2.24H_2O$$

Ettringite + Silicic Acid + Carbon Dioxide + Oxygen → Thaumasite

Both strength loss and heave are associated with thaumasite formation, however, where this is from ettringite alteration it is noted that water is released and the thaumasite structure will occupy 45% less volume than the ettringite host[10]. The known expansive properties of ettringite and thaumasite have led to their formation being identified as key mechanisms leading to sulphate swell failures[11]. There are specific environmental factors required for ettringite and thaumasite to form. These are as listed and further discussed below:

- Access to water
- Temperature
- Humidity
- High pH

Water availability
The 26 or 24 mols of water in ettringite and thaumasite respectively identifies the minerals as highly hydrous[12], with access to external water a crucial part of their formation as well as transport of sulphate ions through the soil[13][14]. The formation of ettringite and thaumasite often occurs in localised low spots, areas of poor drainage or wet winters[11]. Gypsum has a relatively low solubility in water (2.58 g/L) and is considered to not provide enough sulphate ions to result in ettringite formation. However, where water saturates the soil, a mechanism to continuously dissolve and/or transport in the sulphate ions is provided.

Temperature
The ettringite solubility product mechanism is unchanged across the temperature range 5°C to 75°C, with normal thermodynamic behaviour i.e. reactions approximately double in rate with every 10°C increase and vice versa[15].

Thaumasite requires a <15°C environment to form with an optimal temperature of 5°C with the increasing solubility of carbon dioxide at lower temperatures, i.e. CO_2 solubility approximately doubles as water temperature reduces from 25°C to 0°C, is suggested as the likely cause[16].

According to Hunter[12] and assuming all other reactant availability, it can be summarised:

- >15°C. Ettringite is stable and will continue to form.

- Between 10°C-15°C. Assuming both aluminate and silicate are available then ettringite is kinematically favoured and will form first. However, when only silicate is available then thaumasite will precipitate.

- <10°C. Thaumasite is thermodynamically more stable and will preferentially form. Where this low temperature is sustained for long periods then prior formed ettringite will alter to thaumasite.

Humidity
Talluri (2013) suggests that humid environments alone do not have enough availability of water for the ettringite reaction[4]. However, a humid environment followed by a saturated environment would allow for the formation of ettringite[4] and this can be expanded upon as follows. As noted above (see sources of sulphate) where sulphate is sourced from pyrite oxidation in the presence of calcium carbonate this necessitates both air and water and so a humid soil atmosphere promotes this reaction. Pyrites in the natural soil may then preferentially oxidise during damp periods of the summer months when the local water table is lower. This would provide a supply of sulphate ions for subsequent formation of ettringite and thaumasite in the winter months, when increased water inflow saturates this previously oxidised zone[17]. This would meet with Talluri's (2013) suggestion that although ettringite forms in a humid environment, the reactions are less common compared to a fully saturated soil. Furthermore, the high pH and humid environment created during the lime stabilisation process i.e. rotovation of lime through the fill while adding mixing water, would encourage rapid oxidation of pyrite to calcium sulphate[1].

High pH
For a reaction between lime stabilised clay and sulphates in the soil, a high pH is needed[19]. The added lime elevates the pH to 12.4 which increases the solubility of alumina and silica[1]. The high pH also increases the rate at which any sulphide would oxidise to sulphate[20]. Ettringite is stabilised at pH values greater than 12 and becomes less stable at low alkalinity where it will begin to decompose to gypsum[21].

The formation of thaumasite also relies on a high pH of greater than 10.5. The stability of thaumasite is dependent on the pH and once the mineral is formed it can survive at a pH of 7, although as it gets closer to this value the mineral becomes less stable[13].

Sulphate swell tests within the industry and limitations
Sulphate swelling measurements have been undertaken and measured using a variety of methods in research projects e.g. Beetham's Novel swell test[22] and Abdi and Wild's 3-dimensional swell test developed[23]. However, the two main test methods used in industry, and which are stated as suitable in BS EN 16907-4 (2018)[24] are briefly summarised;

- Soaked California Bearing Ratio (CBR) test with linear swell measurement[25]. The lime treated soil is compacted into a CBR mould, cured unsoaked usually for 3 days (although there is flexibility for different periods) before full immersion 20°C water for at least 4 days. Water passes into the specimen via small holes in the base and top metal plates with the linear movement of an unfixed top swell plate recorded. BS EN 16907-4 (2018) requires the test be repeated on at least 3 specimens with failure criteria of average swell >5mm (or 3.94%) or >10mm (or 7.87%) in any single specimen. It is also noted that BS EN 16907-4 (2018) states soaking water should be continuously aerated and soaking should continue for at least 28 days; or until swell ceases. However, these are not requirements of BS EN 13286-47, even in the most recent 2021 revision, and there is no clarity on a method of ensuring water is adequately and consistently aerated.

■ Accelerated swell test (AST)[26]. The lime treated soil is compressed into and then immediately removed from a 50 x 50mm mould. The specimen is cured unsoaked at 20°C for 3 days, then wrapped in a permeable geofabric and soaked in 40°C water for 7 days. The average increase in specimen volume of three specimens is reported with typical failure criteria of >5% noted in BS EN 16907-4 (2018).

Sulphate swell test criticisms

Both standard swell test methods have aspects which may not represent site conditions and therefore could misrepresent the swell potential of a given soil[27].

The tests are performed at temperatures between 20-40°C which does not provide the necessary environment for thaumasite to form. Furthermore, recent studies have shown that when lower soaking water temperatures are used then substantially higher swell occurs. Beetham (2015) reported that reducing the soaking temperature to 8°C after an initial 35 days at 20°C led to a sudden and sustained increase in swell rate of high TPS soils treated with both lime and lime plus GGBS[22]. Newbury et al., compared lime and GGBS treated high TPS soils soaked in 20°C or 10°C, and reported 40% more swell in the lower temperature specimens. UK near surface ground conditions are likely to be closer to 10°C and hence the relevance of soaking at 20°C is highly questionable[28].

Further potential issues relevant to both standard tests are the full immersion of specimens in tap water. Full submersion could preclude an oxidising atmosphere for pyrite oxidation and limit the amount of carbonate available to form thaumasite, especially at 20°C where carbon dioxide is less soluble than at lower temperatures. While use of tap water is convenient and consistent, however, it does not account for groundwater saturated sulphate which is a potential field scenario[13].

The CBR test has been specifically criticised for having a steel mould which could; cause adhesion forces that retard swell; restrict water flow into the specimen[17, 29]. The oxidation of pyrite and the subsequent swell is not accounted for in the CBR test. The test only allows for linear swell to be measured which does not represent the swell on site. Conversely, the AST permits fully free access to water with no confinement which could be too severe to reflect field condition.

These criticisms were highlighted by Snedker's (1996) conclusions that the industry requires a more rigorous test that accounts for typical UK ground temperature and allows for saturation and oxidation of pyrite[29].

METHODOLOGY

The purpose of the test programme was to investigate the degree of swell measured with different sulphate swell test set ups. This included using variations on the soaked CBR and AST, as well as an NTU sulphate swell test (NTU test), which was an adaptation of the method developed by Beetham[22] and is further explained below. There were some deviations to the standard AST method (explained later) and so this will be referred to as a modified AST.

The range of environments considered by the programme are presented in Table 1.

Soil preparation method

Two soil types, i.e. a high TPS and low TPS soil were used in the investigation:

■ Weathered Charmouth Mudstone (part of the Lower Lias group with a high TPS of 2.74% including Oxidisable Sulphate of 0.61%).

■ Mercia Mudstone of weathering grade IVa with a TPS of 0.02% and initial consumption of lime value of 1.5%.

3% by dry soil mass of BS EN 14227-11 category 1 quicklime powder (Tarmac Limbase) was mixed into the test soil using a lab approach considered to reasonably reproduce the site process. The required amount of soil was first passed through a 20mm sieve and spread out in a large mixing tray with the lime evenly spread over the surface. The lime was worked in by repeatedly turning over the material for approximately 15 minutes, after which a consistent appearance to the mixture resulted. The mixing tray was then then placed inside a very large sample bag which, to create a seal, was wrapped around the tray several times. The tray was then left for a 2-hour mellowing period, after which the bag was removed. The material was remixed with the same method and adding room temperature tap water, using a squeeze bottle to evenly spray over the surface, as necessary to condition the material to a target moisture condition value (MCV; BS EN 13286-46:2003) of 10.5. An MCV <12 or lower is noted to coincide with a moisture content at or slightly wetter than the optimum moisture content for 2.5kg compaction[30].

Table 1. The tests and their environments used in the programme. (results in MPa)

| Test | Environment | | Soil Type | Batch Reference |
	Water (10°C)	Confinement		
CBR	Tap Water	Confined	Charmouth Mudstone	CMS_CBR_TAP
	Gypsum saturated tap water		Charmouth Mudstone	CMS_CBR_GYP
AST	Tap Water	Unconfined	Charmouth Mudstone, Mercia Mudstone	CMS_AST_TAP MMS_AST_TAP
	Gypsum saturated tap water		Charmouth Mudstone, Mercia Mudstone	CMS_AST_GYP MMS_AST_GYP
NTU	Tap water Fully immersed	Partially Confined	Charmouth Mudstone	CMS_NTU_F
	Tap water 20mm from base		Charmouth Mudstone	CMS_NTU_B
	Fully immersed and aerated tap water		Charmouth Mudstone	CMS_NTU_A

Following BS EN 13286-2:2012 compaction procedure, all samples were compacted in 3 layers using a mechanical compactor to deliver 2.5kg standard compactive effort. CBRs were compacted into approx. 150mm diameter and 127mm high moulds where they remained for all subsequent curing. NTU and modified AST specimens were compacted into split proctor moulds (approx. 100mm diameter and 115mm high) and samples removed immediately. The standard AST method does require static compression of 50mm x 50mm specimens, however this equipment was not available and so the larger specimen was used. Unsoaked curing was undertaken for 3 days at 20°C with specimens first wrapped in cling film and then sealed in a sample bag.

CBR and modified AST Soaking Arrangements

The CBR moulds were set up in accordance with BS EN 13286-47:2012. Modified AST specimens were set up in general accordance with BS EN 13286-49:2004 except that the soak periods were extended to 14 days when it was noted the samples were still swelling after 7 days.

For specimens soaked in gypsum saturated water, food grade calcium sulphate dihydrate powder (Saint Gobain superfine white) at a dosage of 4.6 g/l was needed for each soaking, the baths were gently stirred daily to help ensure the water remained saturated with gypsum.

NTU sulphate swell test

The aim of the NTU test was to introduce the presence of air, in particular CO_2, to encourage the growth of thaumasite. The NTU test samples were set up in the general arrangement as shown in Figure 1 with 3 soaking water atmosphere variations as summarised in Table 1. After being wrapped in a terram membrane and secured with elastic bands, each sample was placed on a hollow plastic plinth at the bottom of a 5-litre container. The plinth had space to accommodate a porous stone connected via tubing to an aeration pump. With holes drilled into the plinth sides, this provided option to aerate the water. Leighton Buzzard sand was placed around the sample in layers and compacted with a tamping road. The highly permeable Leighton Buzzard sand (1-2mm) provided confinement to the specimen but allowed for the water to access from all sides of the sample.

The three different NTU test set ups were soaked for 28 days at 10°C in a fridge with volume on immersion measurements (in accordance with BS EN 13286-49:2004) taken before and after soaking to compare the change in volume of the sample. A swell plate and dial gauge was used to identify when swell occurred.

Figure 1. Image showing the general set up used for the NTU test
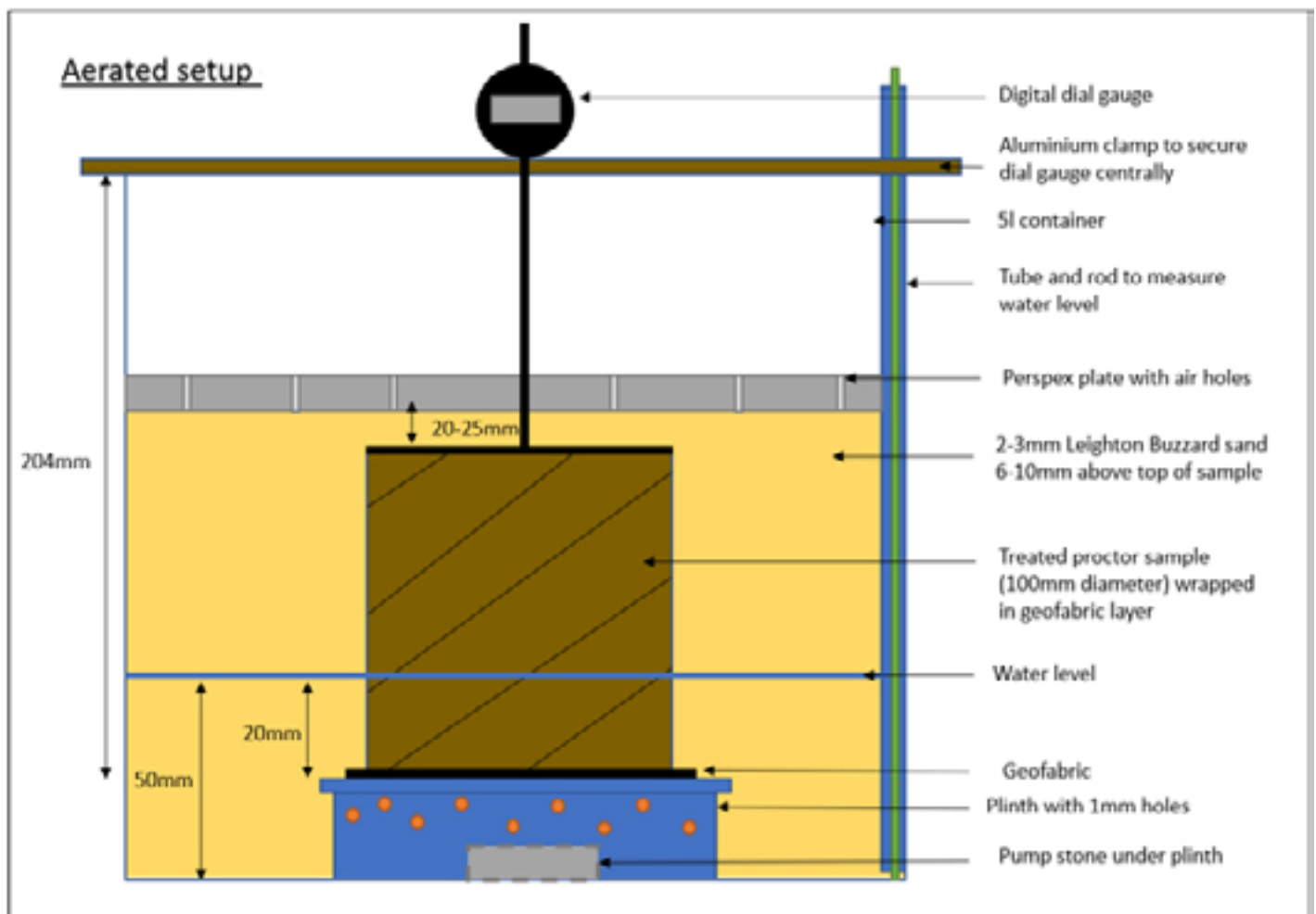
RESULTS

Volume Change % vs Swell Measurements

Figure 2. Graph showing final swell and volume change percentage for the NTU test and soaked CBR.
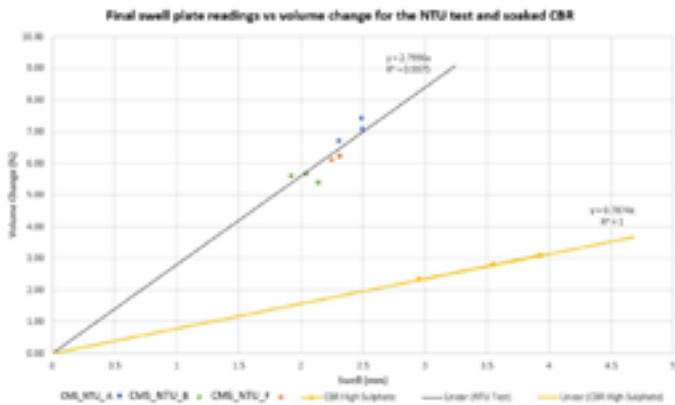

Figure 2 shows the correlation between the final swell plate readings and volume change percentage for the NTU test and CBR test using high sulphate soil. The NTU test had a volume increase of 5.4-7.5% compared to the soaked CBR test which had a volume increase of 2.3-3.1%. This indicates that significant swell is recorded by the NTU test, and this is perhaps related to the easier access to water. This suggests the NTU test is more effective at predicting the degree of risk of sulphate swelling for a scenario where the treated soil is close to the surface and adjacent to regions of high permeability such as a drainage medium.

The coloured dots represent the different test set ups for the NTU test. There is a small variation between the points, however it is not significant enough to conclude that the different test environments cause different amounts of swell.

Accelerated and CBR swell measurements

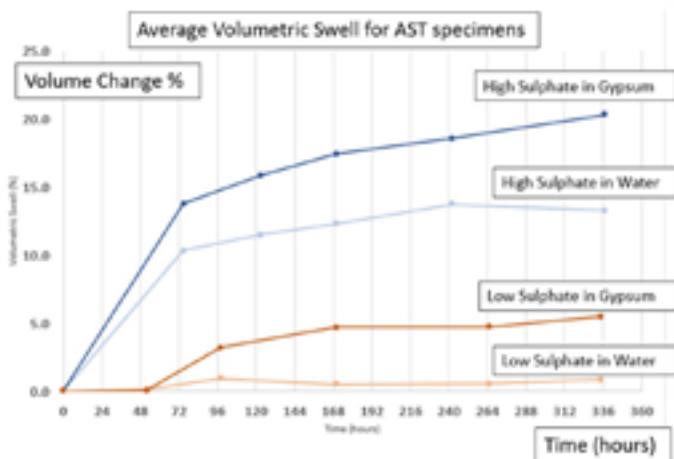**Figure 3. Graph showing the volume change over time for the AST.**

Figure 3 shows the total volumetric swell of the accelerated swell test samples over 14 days. The greatest volume change came from the treated Charmouth Mudstone (high TPS) that had been soaked in the gypsum solution and the final swell measurement was 22%. When comparing this value to the NTU test and CBR, the AST showed significantly higher volume changes and a higher rate of swell. The CBR high sulphate soil samples showed a maximum volume increase of 3.1% which is around a quarter of the volume increase of the same soil mix in the AST samples. This can be attributed to the samples access to water as it can migrate through the samples across their full surface area. The low sulphate soil exhibited minimal amounts of swell after being placed in water. However, the low sulphate soil soaked in gypsum showed an average volume increase of 5% but the swell rate was slower compared to that of the high sulphate soil. This correlates with the results of the high sulphate soil soaked in water as the material swelled by an average of 13%, which is 9% less than that of the same soil mix soaked in gypsum. These results suggest that the introduction of gypsum has had effect on the swell of both the high and low soil samples as sulphate ions have been made available for reaction within the soil samples.

Moisture Content

Figure 4. Bar chart showing the average moisture content for the different tests (including the top 20mm of the samples).
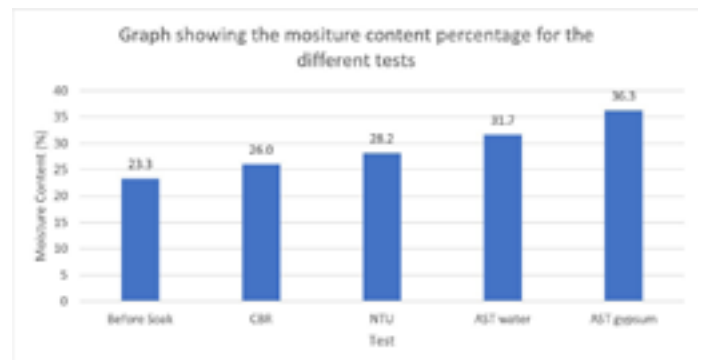
The comparison of the moisture contents of the tests highlights the significance of how the set up restricts or encourages water access into the sample. Figure 4 confirms the expectation that the confined, restrictive samples have a lower moisture content compared to the unconfined samples. On average, the CBR sample had the lowest moisture content proving that the steel mould significantly limits water flow. The NTU test set up allowed 2.2% more moisture into the sample due to water being able to access the whole sample via the permeable sand confinement around the soil. The greatest ingress of water into the samples was found in the AST setups, with the samples soaked in the gypsum-water solution having an average moisture content of 36.3%. This is 4.6% higher than the AST samples that were soaked in only water and 13% higher than the unsoaked soil.

For both the NTU and CBR test, the highest moisture contents were measured at the top 20mm of the samples. This may be due to the potential lack of confinement at the top of the sample which has allowed the top diameter to swell, create cracks and cause water ingress. The AST samples had an even distribution of moisture content throughout the sample, and these were higher than both the NTU and CBR test due to the lack of confinement which allowed water ingress.

Thermogravimetric Analysis (TGA) Results

Figure 5. Graph showing the temperature at which mass is lost for the samples in the different test set ups.
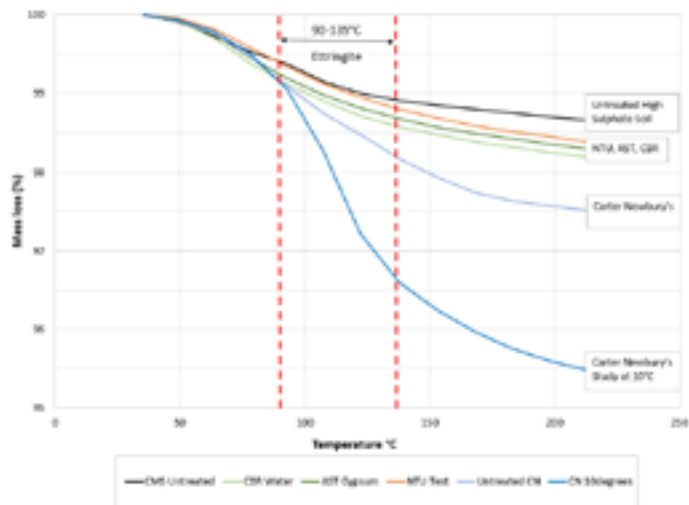
Thermogravimetric Analysis is a technique used to determine the composition of soils by measuring the mass loss at a range of temperatures. A selection of 40g samples, from the different tests, were analysed over a thermal gradient of 30°C for 10 minutes, then increased to 800°C at a heating range of 10°C/minute, then held at 800°C for 60 minutes.

The expansive mineral ettringite is expected to lose mass between 90-135°C[31], and therefore a soil that contains this mineral should present a significant difference in the gradient of the lines for the untreated and treated soil. Figure 5 shows that all three tests investigated follow a similar gradient and there is only approximately 0.5% mass difference between the untreated and treated soil. This small mass loss suggests that only a limited amount of ettringite had formed. Another significant mineral, thaumasite, is expected to lose mass at 50°C[31], therefore soil samples that contain this mineral should present a different mass loss trend than that shown in Figure 5 between 50-135°C. There is not a clear difference in mass loss between the different tests to suggest that one of the tests produced more ettringite and/or thaumasite than the others.

Figure 5 also includes TGA results from a separate study by Newbury et al., which recorded an average 8.1% volume increase in 10°C soaked CBRs on lime and GGBS treated Oxford clay of 2.51% TPS. When compared to the untreated soil in that study, the Newbury et al TGA data on 8.1% swell specimens identifies an additional 2.5% mass loss between 90-135°C suggesting a significant amount of ettringite had formed.

The comparison between the studies is significant as this study is reporting little indication of substantial ettringite in both Charmouth Mudstone and Mercia Mudstone clays, yet the degree of swelling in the tests without restricted access to water i.e. the NTU and modified AST tests were high to very high. This observation on the modified AST tests can be extended further as the low sulphate Mercia Mudstone in tap water did not swell to any appreciable degree. However, when soaked in 10°C gypsum water, swell of around 5% did occur. Across the tests this is suggesting that a sulphate swell mechanism is instigated at this 10°C temperature, but higher swell is not associated with proportionally higher ettringite. Another swell process appears to be at play and as discussed by Beetham[22] this could be due to an ettringite pre-cursor that imbibes water at this low temperature to draw in unbound water but without corresponding growth of crystalline ettringite. This suggestion is tentative and needs more research into swell processes at these site relevant temperatures of 10°C to improve understanding.

CONCLUSION

The results from this investigation conclude that the test arrangement is highly influential on the degree of swell that occurs. There is a positive linear relationship between the access to water and the volumetric change of the samples. Therefore, the greatest amount of swell was measured in the unconfined accelerated swell test, followed by the NTU test and the least amount of swell in the CBR test. The minerology tests indicate that only a limited amount of ettringite formed in the samples and therefore the higher swell is driven by unbound water taken in by the sample. The TGA and X-ray diffraction (XRD) tests (XRD data not presented due to space limitations) also suggest there is no direct evidence of a significant amount of thaumasite growth which was expected at 10°C.

Adding gypsum to the soaking water increases the amount of water taken in by both the low and high sulphate soil samples and therefore increases the volumetric swell. However, the mechanism that encourages this uptake of water has not been identified.

Further research could be conducted on a soil with a higher amount of pyrite to assess the impact of the test environment, in particular the humidity, on the growth of ettringite and thaumasite. This would conclude whether the higher swell is always driven by the access to water or whether the mineralogy plays an equal role. It is clear that the chemical process of sulphate swell at 10°C is not just quantified by the amount of ettringite and thaumasite growth within the soil, therefore further research into these minerals' formation is needed. Also, research is required into the potential ettringite precursors which could account for the high degree of unbound water being drawn into the soil and leading to the high swell rates at site relevant soaking temperatures. Current standard laboratory tests struggle to identify these mechanisms and cannot replicate all scenarios that could occur on site.

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Extracting Minerals . . . Manufacturing Products . . . Supplying Markets

Lime in Precolumbian Construction

Waste and impact

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ABSTRACT

Marco Gonzalez, on Ambergris Caye, Belize, is an ancient Maya site occupied from at least 200 BC until Spanish arrival in 1544AD. This coastal site is distinctive from its surroundings; a raised area, with dark surface soils and littoral forest, which contrast the surrounding mangroves and coastal sands. On-site ecological conditions are thought to have been influenced heavily by ancient occupation, particularly the deposition of waste; 'waste' refers to materials discarded during occupation and also those remaining post-abandonment. Impacts would have been chemical, via waste degradation, and physical, via topographic influence.

A large proportion of on-site waste was lime plaster, used for floors, and stucco on the outside of buildings; lime is a significant on-site waste that likely contributed to onsite ecological conditions. The Maya used a range of raw base materials and aggregates for lime plaster, dependent on available resources and function of the finished product. The chemical compositions and material performances of plasters would have contributed differentially, chemically and physically, to impact.

We aimed to identify the most effective methods for identifying impacts from waste and impact mechanisms. Our research trialled the application of life cycle assessment (LCA) to archaeology, to investigate associations between waste and environmental impact. Though current LCA models are unable to account for some potentially important environmental effects from lime plaster - such as from soil sealing and the contribution of plant macro and micro-nutrients – the method appears to offer great potential for future research, following the development of site-specific models.

THE MAYA

The civilisation of the Precolumbian Maya began at around 1200BC and extended to the Spanish Conquest of Yucatan in 1542AD. Until the 9th century AD, the Maya region (Yucatan Peninsula, Guatemala, Belize, western Honduras and El Salvador) was characterised by numerous but fluid city-states, each under dynastic rule, a span of time known as the Classic period (ca. AD 250 to 830). The Maya 'collapse' refers to the fall of these dynasties in the 9th and early 10th centuries. The spread of Maya centres changed at this time from densely populated major cities (150,000-200,000) and their hinterlands to smaller cities and towns (at most, 50,000) spread widely across the landscape. Aspects of technology changed with the arrival of Europeans (Spanish in the 16th century, British in the 17th), but construction in the Maya area has always been dominated by mineral-based construction materials such as limestone and its derivatives.

USES OF LIME

Nixtamalization

The two major uses of lime among the Maya are nixtamalization and construction. The products of nixtamalization in the U.K. are best known as tortilla chips, although tortillas, tacos, and tamales are becoming much more common. Nixtamalization involves soaking corn/maize kernels in a mixture of lime and water, which is heated until the mixture can, when it is cooled, form a wet flour called masa. The masa can then be formed into tortillas, which are cooked on a griddle, or tamales, which are usually steamed. Tortilla chips require further frying.

Construction

Lime was also used extensively in construction. Archaeologically, kilns are rare, but they have been found at some sites. All over the Maya area, floors, patios, and masonry walls were plastered, as were the great plazas, terraced platforms ('pyramids'), and the civic and ceremonial buildings that the platforms supported. Wood buildings were coated with a clay mixture and then a lime wash. Stucco was used widely in wall and roof ornamentation and could depict rulers, gods, plant and animal motifs, or hieroglyphic text.

Limestone was abundant as a natural material on the mainland, but on the barrier reef islands, only a kind of reefstone was available for construction. Roughly quarried blocks were used in platform construction, but lime was also produced. It is evidence for the production of lime that was recovered as part of a larger study of waste products and their environmental impact at a site called Marco Gonzalez on Ambergris Caye.

MANUFACTURE OF LIME

Dependent on location and supply versus demand, it appears that both shells and limestone were used for Maya lime-making. As an example, at Placencia Lagoon on the coast of Belize, the presence of conch (Strombus spp.) shell, and chemical traces of $Ca(OH)_2$ and $Mg(OH)_2$ are thought to indicate the use of conch (aragonite) and another resource such as sea fans (Gorgonia spp.) or foraminifera shells (high-magnesian calcite) for lime-making, since dolomitic or Pleistocene limestone is not present locally[1, 2]. At the island site of Santa Cruz on Ambergris Caye, where limestone is readily available, and shells are absent in the archaeological deposits, it appears that limestone was prioritised for lime manufacture (mainly calcite, with some high-magnesian calcite or dolomite)[2].

Researchers at Placencia Lagoon, after experimentation and examining archaeological evidence, suggested that lime was produced by using pottery platters on top of which alternate layers of conch shell and wood were placed and then burned until the shell turned white. To powder the burnt shell, their experiments found that pounding was not an effective method, but if the shells were left for a little time, the moisture in the air would have a slaking effect, creating calcium hydroxide ($Ca(OH)_2$). The slaked lime could then have been stored in pottery jars. The researchers believed that this production was for small scale, local use. The shells would have served also as a source of food, being from edible species that are easy to access in a coastal location[1].

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IMPACT OF LIME USE AT A MAYA SITE

Marco Gonzalez, Ambergris Caye

The site of Marco Gonzalez is situated on the island of Ambergris Caye, off the coast of Belize (Figure 1). Archaeological excavations have been carried out intermittently at the site since 1986[3-7], but the majority of data referred to in the analyses presented here were gathered during a field season in 2013.

Marco Gonzalez has a long history. The site dates to at least 200 BC, but the earliest levels are submerged beneath the water table[4-6, 8]. The earliest construction uncovered is an Early Classic (AD 250–500) floor. Other evidence for this period - namely midden (refuse heap) deposits - suggests that people were living at the site throughout the year by this time. The period after this - the Late Classic (AD 550/600–750/800) – appears to have been a time of intensive salt production, which involved the heating of brine to produce salt cakes[9-11]. These activities resulted in a large amount of waste material, up to a metre thick in places. The site was then occupied intensely as a trade settlement, from the end of Late Classic into the Terminal Classic (c. AD 750/800–950/1000). The residents of the site in this period would bury their dead beneath their house floors, accompanied by traded objects that showed a level of wealth[4-6, 8, 12-15]. In the subsequent period (AD 950/1000–1250/1300), the residents constructed further buildings and modified existing construction, as the settlement expanded and increased in wealth, after which the settlement declined[5, 8, 10, 14, 16].

Figure 1. Map showing the location of the site of Marco Gonzalez, Ambergris Caye, Belize.

Buildings at Marco Gonzalez appear to have had residential, civic and ritual functions[4,7, 8]. The building structures uncovered at Marco Gonzalez consist of relatively low platforms (c.30cm–4.2m), constructed mainly of reefstone, and filled with further reefstone, waste materials and large quantities of shell. As elsewhere in the Maya area, these stone platforms would have been topped by perishable structures[6-8, 14]. The floors in the buildings were lime plaster composed of thin layers of mud, grit and lime from burnt shells[7, 8, 11]. The most frequent way that we find lime at the site is the remains of these plaster floors, which can be seen as distinct pale or white layers. Trampled materials from on-site activities - including shell, bioclastic limestone, heated/burned bone (mostly fish), and charcoal - occur between the floor layers[10]. These floor layers can be seen in the walls of the trenches when we excavate and can also be seen microscopically. In excavations and soil micromorphology (microscopic examination of slide-mounted

soil features and layers, in section), lime plaster was recorded as floors, hearths and stucco[10, 11]. Soil micromorphology of Early Classic (AD 250–500) lime plaster floors has shown evidence of burning including household fireplaces that are suggested to have been used for food preparation, and perhaps the cooking or smoking of fish[10, 11]. Later evidence shows plaster floors used in salt production activities.

Soil micromorphology has indicated that Marco Gonzalez's lime plaster floors were composed of a range of materials and tempers; non-calcareous tidal flat sediments, rich with silica sponge spicules, is one example of temper[11]. The micromorphology has suggested a possible shift in plaster composition over time, with increasing calcium content and shell inclusions, moving from the Early Classic (AD 250–500) to the Late Classic (AD 550/600–750/800)[10, 11]. SEM/EDS composition results for slide-mounted plaster thin sections include a range of values: Ca 4.55–65.5%; Si 11.9–19.4%; Mg 2.08–14.1%; Al 0.56–13.9%; Fe 0.42–5.49%[11]. The variation may be explained by original composition or by later processes such as burning activities or leaching via weathering; lime dissolution is visible microscopically, with recrystallisation in the levels below[10, 11].

On-site environment

The local environment of the Marco Gonzalez site – like other ancient sites on the island – is diverse broadleaf vegetation and fertile dark soils that contrast the caye's sandy sediments and coastal forests and wetlands. Fruit trees and crops grow on the island today, in areas of past occupation, which would not be possible on un-altered caye sediments[8, 10]. Similar characteristics have been noted in other Maya areas (e.g. Stann Creek District:[17]). The vegetation at Marco Gonzalez appears, to some extent, to reflect ecological requirements, for example soil depth and nutrient availability[8, 10]; conditions that have, to some degree, been created by the archaeological site.

The soils at Marco Gonzalez consist firstly of surface soils (Ah1 horizon) that are highly organic (26.9–28.0% LOI), mercury-rich (max. 467 ng g-1), phosphate-rich (11.4 mg g-1 in one location), and lower in pH compared to other levels (pH = 7.9). The chemical properties of the surface soils can be attributed primarily to vegetation, but they do also contain material from ancient settlement, including fragments of lime plaster, shell, reefstone, burnt bone and pottery. Plants appear to be recycling materials in the deposits below, by rooting in the archaeological levels[10, 11, 18]. Underneath the surface soils is a 'Maya Dark Earth' deposit. Dark earths are buried soils that are found in areas of past human settlement and are frequently more cultivable than surrounding soils. The dark earths are based on weathered lime-based building materials; they have high levels of calcium carbonate, which can be attributed to reefstone, lime plaster and ash waste. The dark colour of these soils can be attributed to very fine charcoal, but also other occupation waste[10, 11].

Research at Marco Gonzalez has demonstrated a relationship between present-day soil mass, soil nutrient status, and past settlement; it appears that materials from past settlement can be linked to soil formation, and consequently present-day landscapes that differ from expected island conditions[17, 19, 20]. When archaeologists excavate, we normally characterise layers in the soil as 'features', objects that we find as 'artefacts', and plant and animal remains as 'ecofacts'. At Marco Gonzalez we have instead viewed all of these materials as 'waste', some of which have decayed and contributed to the development of fertile soils; one of these wastes is lime.

LIFE CYCLE ASSESSMENT

Life cycle assessment (LCA) is a system-based approach that accounts for environmental impacts for inputs, outputs and flows (raw materials, energy use, emissions and waste products) of a defined system. According to ISO14040[21], LCA:

'addresses the environmental aspects and potential environmental impacts (e.g. use of resources and the environmental consequences of releases) throughout a product's life cycle from raw material acquisition through production, use, end-of-life treatment, recycling and final disposal (i.e. cradle-to-grave)' (p. v).

LCA is used commonly for industrial or product-centred assessments (e.g. concrete aggregates[22]; cement manufacture[23]; food products[24]). The results are expressed as categorised potential environmental impact indicators that permit comparisons between and within systems. The results are intended to provide overall estimates that highlight areas with the greatest impact potential that can then be targeted at higher resolution with other tools. LCA follows four defined phases: Goal and scope definition, to identify the breadth and depth of the study; Inventory analysis, to quantify input and output data; Impact assessment, to convert the inventory's results into impact potentials, to assess environmental significance; Interpretation, to summarise, evaluate and conclude[21].

The life cycle inventory (LCI) is the data collection phase that quantifies the system's processes. Data are collected for: elementary flows (raw material resources, emissions to the environment, other environment interactions such as land use), product flows (goods and services), waste flows, and any other appropriate information[25]. Data are allocated between inputs and outputs. Inputs include product flows (materials, services, parts, consumables) and elementary flows (from nature: ground, water, air, biosphere, land). Outputs include elementary flows (emissions to air, water and soil), waste flows (solid, liquid and gaseous, managed in the technosphere) and product flows (valuable goods and services)[25].

In the life cycle impact assessment (LCIA) the inventory flows recorded in the LCI are assigned to relevant impact categories[21, 25, 26]. The LCI results are converted to an equivalent value by multiplication with a characterisation factor that 'expresses how much that flow contributes to the impact category indicator'[25]. The characterisation factors are formed from models that reflect environmental mechanisms such as the uptake of different substances in different environments[26]. The sum of each impact category is calculated and given as per kg elementary flow. These sums are known as midpoint impact indicators[25].

The results from the LCIA produce impact potential indicators[21, 25]. The results do not indicate threshold exceedance and are also limited by the quality of the LCI data and the specificity of the characterisation models [21, 26]. The LCIA results do, however, permit comparisons within – not between – the impact categories[25]. This facilitates the identification of system areas with the highest potential for environment impact.

LCA at Marco Gonzalez

We applied LCA at Marco Gonzalez to examine the impact of waste on the local environment. We define 'waste' as the material remains of human occupation; materials discarded during occupation and also those remaining post-abandonment of the settlement. Our aim was to use LCA to interrogate our data and to indicate wastes and impacts

that could then be investigated in further detail with other methods. To our knowledge, this was the first application of LCA to archaeological data. As a result, the application of LCA was experimental, to determine the value to archaeological datasets and research at Marco Gonzalez. The benefits of LCA were anticipated to include its ability to analyse a multitude of system components, its common application to modern waste scenarios, and its flexibility in the absence of a complete dataset. In the absence of a pre-existing archaeological LCA toolkit, and with the investigations at Marco Gonzalez in the early stages, the LCA was applied as a pilot study with a simplistic analysis, but it provides a starting point for future development of methods[27]. The analysis followed standard LCA terminology and procedure where possible, to evaluate the method with archaeological data. The LCA was performed manually because the system-specific variables – materials and activities – are not available in LCA software[27].

The system boundary of an LCA defines the processes that are included in the analysis, ideally all of which fulfil the system's function. Waste and any post-discard changes occur at the end of a life cycle, as part of a larger system. At Marco Gonzalez, waste discard and transformation (decomposition) were included within the system boundary, with preceding activities positioned outside the system boundary, in association. The emissions (elementary flows) from waste decomposition were modelled as leaving the system and entering the ecosphere (natural environment - soil, water, air - with which the system interacts). This follows unmanaged waste disposal guidelines[25] and approaches that have been applied to landfill (e.g.[28]).

System inputs were characterised as the waste materials deposited on site. The waste was divided into materials: pottery, charred (carbonised) organics, ash, human remains, fish bone, shell, coral, lime plaster, obsidian, chert, reefstone, and human waste. Much of the waste deposited on site is likely to have been affected by degradation in a tropical environment, but the quantification methods could only account for material that had not decomposed beyond recognition at the time of excavation. The environmental impact scenario that we tested was one whereby all materials found in our excavations hypothetically decomposed into singular element emissions based on their composition, that were then emitted to the local environment. The idea was that the wastes encountered in excavations would retain some relationship with the original profile, and that the model can be modified once we have a better understanding of on-site decay and decomposition conditions[27].

A critical part of an LCA is the definition of the functional unit, which is the scale to which all data are adjusted during quantification, to facilitate comparison[25]. The function of the system was defined as 'the accumulation and degradation of occupation waste'. The functional unit (FU) was defined spatially to examine the effect of waste disposal within a demarcated area, to complement the way in which archaeological data are collected via the excavation of trenches. The footprint of these excavated trenches informed the spatial unit. All data were scaled to the smallest trench area, measuring 1.62 m^2, to avoid any assumptions from upscaling[27].

The life cycle inventory required the quantification of waste mass. For lime, volume of waste was calculated from the drawings of our trench walls that we make as standard during excavations; lime that was observable. For the purposes of experimentation, the lime layers were assumed to extend across the trench because of its small area[27]. At depths where lime layers had not been observed during excavation,

soil micromorphology slides (microscopic thin sections of soil levels) were used to estimate lime thickness and then calculate volume. Fragments of plaster that had been recovered during the excavations were used to calculate a general density for lime plaster that could be used to convert overall volume of lime plaster to mass. This density was 0.72 g/cm³[27].

In the absence of decomposition models, emissions from waste degradation were inventoried as single elements to create a foundation that can be modified when on-site decomposition is better understood (Table 1). Bisinella and colleagues[29] also inventoried single elements in their LCA of modern waste management. The nature of the 2013 excavations did not permit the sampling of each lime plaster deposit for composition. A general composition was applied, therefore. The problem with this composition is: variable amounts from each stage of the lime cycle were likely present in the plaster; constituent composition may have changed over time, as outlined previously. XRF analyses were conducted on larger fragments of lime plaster (as well as SEM/EDS analyses of plaster within the microscopic thin sections) but, with evidence for later weathering and burning processes, the original composition of plaster could not be ascertained confidently for all levels. An average composition was calculated from all available data and applied across the LCA. This composition was 31% calcium and conservative estimates for the other major elements: Si 10%; Mg 7%; Al 6%; Fe 2% (Si and Al could not be included with the available characterisation factors)[27].

Table 1. Life cycle inventory data for lime plaster, for all elementary flows recorded for this material (**highest value for the period, across all waste materials).

		Period			
		Terminal preclassic (100 BC–AD 250)	Early Classic (AD 250–500)	Late Classic (AD 550/600–750/800)	Postclassic (AD 950/1000–1544)
Mass (kg)	Total mass	0.000	58.320	828.144**	0.000
	Ca	0.000	18.079	256.725**	0.000
	Mg	0.000	4.082**	57.970**	0.000
	Fe	0.000	1.166**	16.563**	0.000

The impact categories were selected from standard LCA categories relevant to local impact: eutrophication (marine, freshwater), human toxicity and ecotoxicity (terrestrial, marine, freshwater)[25], with the additional category of total solids. These were the only impacts that could be measured with available data. Owing to this project being the first experimental application of LCA to archaeological data, we used existing conversion factors, or impact models. These impact models can then be adapted once we have a better understanding of the onsite environment. The LCI results were multiplied by the appropriate characterisation factor to produce the LCIA results. The LCIA applied characterisation factors mostly from ReCiPe 2008, since this version contains more characterisation factors for single elements than later versions. Where characterisation factors are available for 'emissions

to forestry' or to 'agricultural soil', then forestry options were selected, since this scenario more closely represents what we believe occurred on site i.e. less intensive land management. For ReCiPe factors, the egalitarian perspective characterisation factors were used (as opposed to individualist or hierarchist) because this is the most precautionary approach that uses the longest time-frame for environmental impact and also accounts for more non-standard types of impact[27, 30-32].

With the impact categories that we could apply in the LCA, lime could only be attributed to total solids (total mass). Lime plaster was the second largest mass overall, after limestone, and lime plaster was particularly dominant in levels dated around AD 250 to 800. Lime plaster, however, is easier to identify and quantify than some of the other materials in the deposits. In terms of soil building and landscape changes at the site, total mass could potentially be important, since mass might contribute to soil mass, assisting the retention of nutrients, and counteracting erosion. Alternatively, mass may have contributed to topographical changes, which might also impact erosion and other factors[27].

Potential additional impacts of lime plaster

It's important to consider that lime plaster may have had additional impacts that could not be measured by the LCA. The first is the soil sealing-effect of plaster floors, causing disruption to water infiltration. The caye's natural sediments are loose and open, with a high percolation rate and limited surface runoff, except in extreme rainfall[33]. The characteristics of the natural caye sediments, therefore, provide conditions for the movement of decomposition substances down to the water table. Percolation is likely to have been reduced by plaster floors, which are less permeable than the caye's sands. Materials buried beneath plaster floors, therefore, are likely to have experienced lower levels of disturbance, which is likely to have modified degradation processes. For burials, for example, variables such as temperature, soil texture, geology, rainfall, moisture, pH, microbial activity and oxygen availability will impact decay rate and the movement of decay products; for example, sandy soils assist decomposition via gas diffusivity[34, 35]. The plaster floors that sealed burials would have impacted these decay variables. The floors would have also – in the short term – inhibited interactions with aboveground vegetation. Without interference, the decomposition products of burials can enter the groundwater and cause issues such as nitrification of water sources and pathogen contamination, which can be exacerbated in tropical conditions[35]. Soil sealing disconnects soils from surrounding ecosystems and may reduce chemical reactivity, decrease soil moisture, decrease biomass, diminish groundwater recharge, and increase ponding, erosion and contaminant transfer in adjacent areas[36-39]. In the tropical climate with heavy rainfall, the potential for erosion in adjacent areas, as the result of sealing, is pertinent to Marco Gonzalez. There is some evidence at the site for movement and burying of sediments, which may have been the result of erosion. This evidence has been found in core samples and in soil micromorphology samples[10, 11, 13, 27].

Decayed lime could also have contributed to plant nutrients. Lime plaster in the Early and Late Classic periods was one of the biggest potential contributors of calcium and magnesium to the deposits (Table 1), although it is noted that nutrients must be mobile in the soil. The potential pH-increasing effect of lime could also have had the capacity to affect plant growth and the retention and availability of major and trace elements[27]. Iron and manganese, for example, decrease in availability as pH increases, but molybdenum increases[40].

Extracting Minerals . . . Manufacturing Products . . . Supplying Markets

Nitrogen has a lower availability below pH 5.5-6, but also declines above pH 8 [40], and in strongly alkaline soils the solubility of soil organic matter is increased [40]. Inorganic phosphorous is generally poorly mobile as it is highly reactive with a variety of soil constituents, but in tropical and subtropical calcareous soils, phosphorous retention is markedly increased, resulting in lower plant availability [41]. These effects will need to be considered in future LCA iterations.

CONCLUSIONS

The LCA has certainly indicated areas for further research. Accurate models for the environmental impact of waste will need to understand the fate of decomposition products and whether they remain in situ. Future research will seek to create more site-specific models for decomposition with a better understanding of decay emissions and temporal and spatial factors. This will require a better understanding of factors such as soil microbial communities, hydrology, soil temperature, aeration and pH. Our additional aims are to develop more site-specific LCA characterisation models to examine additional, relevant impacts such as soil organic carbon, land use and plant nutrients.

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Abstracts for Symposium Presentations

THE PATH TO DECARBONISATION FOR THE LIME INDUSTRY

Dr Humbul Suleman, Saisurya Pothukanuri, Harsha Vardhan Pinninti, Parth Bharatkumar Patel, Faizan Ahmad – Teesside University

To meet the UK's pledge for a net zero economy by 2050, industries are undergoing massive changes to reduce their carbon dioxide emissions and the lime sector is not an exception. With an intrinsic production of carbon dioxide during its manufacture, the sector struggles to decarbonise its set of activities starting from mining to end-user wastes. This study provides a systematic review of all the areas that can produce direct and indirect carbon dioxide emissions. The emissions estimates from the sector are assessed and divided broadly into sub-sectors; production, transportation, usage and end-of-life. The study also provides various strategies and timelines for the decarbonisation of the sub-sectors via various active and passive pathways, which include process change, efficiency improvement and emissions capture. Sequestration options like carbon dioxide transmission networks versus onsite mineralisation (with perspectives of sales, utilisation and storage) are technically compared.

PARTICIPATION IN THE PEAK DISTRICT ZERO CARBON CLUSTER OF THE HYNET PROJECT

Andy Jackson – Lhoist

HyNET is an Integrated CO_2 reduction project involving carbon capture and storage (CCS) + Hydrogen Production in the North West of England. At the centre is a blue H2 production facility at Stanlow (Essar) using Johnson Matthey technology with capacity for 3TWh low carbon hydrogen. Furthermore, a hydrogen network is planned, provided by Cadent. Finally, CCS in Liverpool Bay at the former gas fields of ENI – with capacity of 10 MT from a proposed pipeline.

The Peak Cluster comprises 2 to 2.5 million tonnes/yr CO_2 from the 3 cement/lime companies present in the region. The production of these materials is the largest single contributor of CO_2 emissions in NW England, 25% of the region's entire CO_2 – so it is critical that it is covered within the decarbonisation plans. The goal is to develop a shared CO_2 pipeline transporting captured CO_2 to the core HyNet system for permanent storage. The initiative is a collaborative effort between companies, addressing the challenges of dispersed sites through partnership - recognising infrastructure needed and a proactive push towards government for support.

Clearly there are challenges connecting remote sites in the Peak District, for example pipeline permitting; plus, all carbon capture projects require focus around capture technology & energy requirements. Nevertheless, these issues can be overcome given the overarching goals, commitments and fundamental need to act.

Ultimately the benefits will be that several million tonnes per year of CO_2 can be captured via integration with a highly developed network / cluster in the North West. The activity is clearly aligned with Global, National, Societal and Company goals around sustainability and would lead to the long-term production of low carbon mineral products, potentially carbon negative with use of low carbon fuels ("BECCS").

PRACTICAL ASPECTS OF TRIALLING HYDROGEN AS PRIMARY FUEL FOR LIME MANUFACTURING

David Wilson – Tarmac Lime

This project aims to use of hydrogen as an alternative fuel for high calcium lime manufacturing. Natural gas systems are well established in the lime sector, both in terms of supply and process design and management. Alternative gas feeds will need to be considered not only for the possible impact on product quality, but also on operational processes, process engineering, health and safety, environmental management and workforce skills and competencies.

All lime is manufactured through high temperature kiln processes whereby calcium carbonate – from limestones or chalk - is heated to drive off carbon dioxide. This chemical reaction occurs at about 1,000°C and is known as calcination. The residence time of the stone in a kiln varies depending on the type of kiln and type of final product required, but can be anything between six hours and two days.

In the UK, high purity limes are required to service diverse markets, such as in mortars and renders, iron and steel manufacturing, soil stabilisation, emissions control, water and wastewater treatment, and pharmaceuticals and cosmetics. To meet the demands of these markets, UK lime is manufactured from high purity limestone. Natural gas is the preferred fuel as it introduces few impurities and is readily available through the gas transmission system. It also has lower carbon emissions when compared to solid fuel alternatives such as coal or lignite. There are no examples of replacement gaseous fuels for natural gas that would ensure maintenance of the quality of the high calcium lime product required in the UK.

In the UK, lime is manufactured using two types of gas-fired kilns; vertical shaft kilns and parallel flow regenerating (PFR) kilns. PFR kilns are widely considered to be the most energy efficient. Vertical shaft kilns use similar technology and processes but are less efficient. However, by their nature, vertical shaft kilns are more challenged by hydrogen fuel than parallel flow regenerating kilns, given counter-current nature of the heating and the limited fuel and air mixing in vertical shaft kilns and the importance of this mixing to product quality.

Key challenges to be addressed to convert vertical shaft and PFR kilns to hydrogen include:

- Gas density/calorific value, combustion stoichiometry, and flame speed and temperature and the impact on kiln performance and product quality

- NOx, other emissions to air and exhaust gas moisture content, including the formation of emission products in the kiln, and the impact on emissions control systems

- The long term embrittlement and degradation of materials in kiln systems, including damage to refractories.

As lime manufacturing is permitted under the Environmental Permitting Regulations, demonstration of hydrogen fuel in lime manufacturing offers an environmentally robust means to assess technology feasibility within the sector.

This project is funded by the Department for Business, Energy and Industrial Strategy (BEIS) Energy Innovation Programme. The project is managed by the Mineral Products Association (MPA) and the British Lime Association (BLA), and Tarmac are providing the demonstration site for the project.

By delivering projects through the BLA, the project outcomes can be shared widely across the sector. The BLA is a member of the European Lime Association (EuLA) and the International Lime Association (ILA) ensuring that UK technologies and best practice will have the widest possible reach.

PRODUCTION OF SLAKED LIME FROM LIMESTONE AT ATMOSPHERIC CONDITIONS AND WITHOUT THE RELEASE OF CHEMICAL CO_2

Theodore Hanein, Marco Simoni, Chun Long Woo, John L. Provis and Hajime Kinoshita – University of Sheffield

The production of lime normally requires the calcination of limestone (mainly $CaCO_3$) which contributes to carbon dioxide (CO_2) emissions that are changing our climate. Moreover, the calcination process requires high temperatures (~900°C).

A novel low-temperature process for the production of slaked lime is presented whereby the CO_2 is directly sequestered in sodium carbonate; thus, avoiding any requirement for post-combustion capture. The limestone is reacted with an aqueous sodium hydroxide solution by mixing under atmospheric temperatures and pressures. Reaction progression, using crushed limestone, is studied through X-ray diffraction and thermogravimetric analyses.

A range of conditions to achieve high conversion rates are identified and the reaction is fast (in the order of a few minutes), while the silica impurity in the limestone remained inert. It is also demonstrated that the products ($Ca(OH)_2$ and Na_2CO_3) can be separated through selective dissolution.

This technology can enable net-zero production of lime as well as combine the lime and sodium carbonate manufacturing processes into a single low-temperature process.

INVESTIGATING THE FEASIBILITY OF CARBON CAPTURE OPTIONS FOR THE LIME INDUSTRY

Tom Cutler – Newcastle University

There are a wide range of possible options for carbon capture from point sources, some of these are mature technologies such as amine absorption and others such as algae-based carbon capture are relatively new concepts. This report aims to investigate the feasibility of various options available for use in a lime kiln with particular emphasis on novel biotechnologies. There is potential for biotechnologies to play a significant role in the decarbonisation of major global industries that are aiming to reduce their greenhouse gas emissions. The carbon capture options included in this research are amine absorption, membrane technology, benign solvent assisted by carbonic anhydrase, microalgae and oxyfuel kilns. The study will investigate the practicality of these options for implementation at a lime kiln and develop a definitive list of the limitations and possible advantages of each technology. The preliminary findings from the initial literature review are that the cost of conventional amine absorption carbon capture is too expensive for the lime industry unless significant heat recovery can be implemented for solvent regeneration. The other technologies included in this study such as membrane capture, absorption assisted with carbonic anhydrase and algae-based capture have not been extensively developed on an industrial scale. Therefore, further research into novel biotechnologies is the necessary next step to determine if they are feasible and affordable carbon capture options.

TECHNICAL AND ENVIRONMENTAL ANALYSIS OF CALCIUM LOOPING CARBON CAPTURE FOR ROTARY KILN LIME PLANTS

Angela Rolfe, Caterina Brandoni, Neil Hewitt, Ye Huang – Ulster University

Globally, cement consumption is second only to water. The cement production process emits large amounts of CO_2 through both calcination and fossil fuel combustion, and accounts for approximately 5% of anthropogenic GHG emissions. Reducing CO_2 emissions from the cement industry is a step towards net zero carbon.

This work focuses on the technical and environmental evaluation for the integration of three calcium carbonate looping (CCL) technologies, i.e., Tail CCL with direct heating, Tail CCL with indirect heating and integrated CCL. These technologies are compared against an oxy-fuel combustion and a base case cement plant. The technical analysis was carried out using the inhouse ECLIPSE software and the SimaPro© software was used for the environmental assessment. Data for the modelling was supplied by project partners, databases, and literature where necessary. The ReCiPe© endpoint method was used for assessment.

The main conclusions are that all carbon capture technologies studied lowered the environmental impact of the cement plant, compared to the base case plant. Both Tail CCL technologies used more resources than the integrated CCL process, and had increased emissions, however, the Tail CCL processes generated much more heat than was suitable for electricity generation, which could be used for the utility consumption and to export to the electricity network. Thus, reducing their environmental burden in line with that of the integrated CCL process. Although the oxy-fuel plant captured 100% of the carbon emissions from the cement plant. There were indirect carbon emissions associated with the increased electricity consumption.

SITE RELEVANT RISK OF SULPHATE SWELL IN LIME STABILISATION

Carter Newbury, Paul Beetham, David Belton and Yasameen Al-ameen – Nottingham Trent University

Where elevated quantities of sulphate are present, expansive minerals such as ettringite may form following lime treatment of earthworks materials. This can cause a high degree of swelling with potential to damage overlying structures. Prior research has established that the degree of sulphate swell may be reduced by partially substituting lime binder with GGBS and using longer mellowing periods. Therefore, this laboratory study used 2% quicklime with 6% GGBS and a 24 hour mellowing period to stabilise a high sulphate soil. Experience from sulphate swell failures in the UK indicate that laboratory test conditions,

e.g. 20°C soaking water, do not reflect the onsite environment coincident with reports of very high swell and some studies have suggested field temperatures <15°C may result in thaumasite growth to cause further swell. This may prevent standard laboratory tests from determining the true risk of swell. Therefore, this study used a standard test method (the soaked CBR test) but compared swell from soaking water temperatures of 20°C with a more site realistic 10°C. Findings show average swell in the 20°C specimens of 5.7mm, however, the 10°C specimens experienced nearly double the amount with an average of 10.3mm. Thermogravimetric analysis indicates ettringite growth is the primary cause of swell and that ettringite precipitation is more extensive at the lower temperature. No evidence of thaumasite was found. It is concluded that caution should be taken when using laboratory tests performed at 20°C to predict the in situ performance of a lime treated material.

INCREASING THE TECHNOLOGICAL PERFORMANCE OF CHALK-DERIVED PRODUCTS FOR THE WATER INDUSTRY

Dávid Kocsis and Christopher Meyer - Singleton Birch, Nathan Lawrence and Jay Wadhawan – University of Hull

Discoloration of potable water in distribution systems is due to the presence of iron and manganese oxides. The latter, in particular, coat water pipes and are hard to dislodge, except through "hydraulic shocks". Sources of manganese include its inadequate removal within water treatment plants, or through oxidation of trace Mn^{2+} by chlorine or by bacteria, leading to MnO_2 pipe deposits. Lime, derived from quarried stones, can contain manganese, and this, when added as a pH modifier during particular points of the water treatment process, can introduce manganese into the water distribution network. This presentation provides an overview of manganese in limestones and their derivatives (lime and hydrate), it characterises the chemistry required for the reduction of manganese in these materials, quantifies the removal mechanisms, and illustrates a process to develop "manganese-inactive" lime products.

LIME FOR MORTARS & RENDERS

Dr Richard J Ball – University of Bath, Giovanni L. Pesce – University of Northumbria, Manuel Nuno, Cristiano Figueiredo, Carla Florbela Ferreira Pinto da Silva, Martin Ansell – University of Bath, Adel El-Turki, Geoffrey Allen – University of Bristol

Air quality is an important issue facing society and lime mortars have a potential role as a material in helping to mitigate against pollution both indoors and outside. The interaction of the outdoor pollutants NOx and SO_2 will be discussed and their interaction with lime-based materials. The development of photocatalytic lime-based coatings which actively neutralise pollutants will then be presented in addition to the role of these materials for protecting heritage buildings. The results of a study employing X-ray photoelectron spectroscopy will be used to elucidate the reaction mechanism between lime, TiO_2 and SO_2. Indoor air quality, sick building syndrome and common indoor pollutants will then be introduced. The ability of interior materials to mitigate the effects of indoor pollutants will be addressed and a comparison made between the behaviour of lime and other materials commonly found in the indoor environment. Studies of the adsorption and desorption phenomena were carried out using a bespoke test rig. Lime was shown to have the greatest capacity to regulate volatile organic compounds (VOCs) but did not permanently sequester them.

IMPORTANCE OF MORTAR SUBSTRATE INTERACTIONS IN LIME MASONRY STRUCTURES

Tugce Busra Su-Cadirci, Julianaa Calabria-Holley, Richard J. Ball – University of Bath

The effect of dewatering and brick dust additions on hydrated lime mortars has been investigated for conservation applications. The water sorptivity character of substrates used with mortars is one of the most significant factors that influence the bond strength. For example, high-water retaining mortars in contact with low sorptivity substrates can result in a weaker bond at the interface. However, the connection of a freshly mixed mortar to a dry substrate can cause a spontaneous process, dewatering. The dewatering modifies the water/binder ratio and water retaining character of the mortar. In addition to dewatering, this study investigates brick dust additions to hydrated lime mortars for improving their suitability for use on site. The effect of brick dust additions on short and long-term (ageing) effects have been studied by comparing non-dewatered and dewatered mortars. Mortar specimens were prepared in the ratio of 1:1:2 (Lime:Brick dust:Sand). Results demonstrate that setting time, time to dewater, consistency, porosity, and water penetration depth decreased due to mortar matrix densification. The compressive strength, carbonation depth, and transfer sorptivity also increased. Mortars with higher brick dust contents exhibited a greater water loss due to the increase of transfer sorptivity, while the lowest porosity was found in 6-month-old mortars (compared to those of an earlier age). Improving workability and optimising mortar-substrate interactions of hydrated lime mortars can promote and improve their use on site.

THE USE OF ORGANIC ADDITIVES FOR IMPROVING THE CHARACTERISTICS OF LIME

Cecilia Pesce and Giovanni Pesce – University of Northumbria

Understanding the physicochemical interactions of lime with different organic additives is an essential step toward the tailoring of the properties of lime for specific applications. Organic compounds are commonly used in a number of applications where lime is the main ingredient. In construction, they have a long history in mortars and renders production, and in the modern industry are commonly used as additive in cementitious materials.

Since the characteristics of organic molecules can widely vary, their effects on lime can be likewise broad. Organic molecules are known to affect properties such as the rheology, microstructure, reactivity, setting, and durability of lime and lime mortars. However, the exact knowledge of the interaction between lime and the organics is very limited and a number of relevant questions remain unanswered, as the very nature of the interaction can be quite complex. If the use of organic additives in improving the characteristics lime could be fully exploited, a simple addition of an organic compound – which might be as affordable as table sugar – to a lime mix would be a straightforward, cost-effective, and easily scalable solution to optimise lime performance.

In our laboratory-based research, we aimed at assessing and monitoring the effects of ten different organic compounds (including sugars, biopolymers and low-priced manufacturing by-products) on the micro- and macro-characteristics of portlandite, and the physico-mechanical properties of the mortars that can be produced with such limes, using various analytical techniques and experimental setups.

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The results show that dissolving compounds such as sucrose (table sugar), inulin (plant and grains extract), and lignosulfonate (wood pulping by-product) into the slaking water, results in significant crystallite size reduction and increase in specific surface area of lime particles, and that such characteristics are maintained nearly constant after up to six months of storage underwater.

LIME STABILISATION IN MAJOR CONSTRUCTION PROJECTS

Dr Paul Beetham – Nottingham Trent University

Lime stabilisation has history of use in highways applications and is gaining greater recognition for the benefits it brings to earthworks in wider civil engineering projects. Experience from highways projects has provided the stabilising industry with knowledge on how to achieve good performance from a range of fill types sourced across different UK geological formations and also how to identify and manage risks from deleterious reactions such as sulphate swell.

However, there is a need to be ever mindful that different types of project have different challenges and engineering performance requirements. For example, the fill for HS2 rail embankments requires high small strain stiffness (Gmax) durable to a 125-year design life so that trains may safely operate at high speed. Lime stabilisation is used to improve site won cohesive fill to this otherwise unobtainable condition.

A case study is used to demonstrate that where infiltration SUDS (sustainable urban draining schemes) are installed into lime treated earthworks there is a risk of high pH leachate contaminating river water. Previous industry understanding was that lime leachate is a negligible risk, but our past experiences are based around careful drainage of rainwater away from earthworks and awareness of the importance of appropriate drainage design is fundamental to avoiding future problems.

By considering past experiences and research to establish a best practice approach to 'business as usual' testing, alongside an innovation / R&D programme, HS2 is well positioned to take optimal advantage of lime stabilisation benefits while managing the identified risks.

HYDRATED LIME IN ASPHALT – RESULTS FROM RECENT FRENCH SECTIONS

Didier Lesueur, P. Métais, P. Pibis, S. El-Bédoui, H. Ruat, S. Bouron and F. Hammoum – University of Lille

Results from 7-years and 5-years of monitoring two sections of highway, are described, with and without the use of hydrated lime in the asphalt mixtures.

A semi-dense asphalt concrete was laid in 20 sections, with and without hydrated lime, in the Vosges region of France – a mountainous region characterised by cold winters and significant elevation. These sections have been monitored for 7-years.

Five sections, with and without hydrated lime, have been monitored in the coastal climate of the A84 Highway in Normandy in the North of France. These were also constructed with a semi dense asphalt, and have been monitored for 5-years after initial testing.

Visual observations and mean texture depth measurements of the sections in Vosges showed that the mixtures with hydrated lime experienced less ravelling/stripping. The damage state of hydrated lime mixtures after 6-years was the same as for non-hydrated lime mixtures after 3-years.

Testing of the asphalt on the A84 in Normandy showed that the hydrated lime additions slowed the bitumen ageing and enabled the mixture to maintain good resistance to moisture damage even after 5-years. As yet no surface damage is visible, although a slightly higher texture depth has been noted on untreated sections.

Monitoring of both sites is ongoing.

MANY AND VARIED INDUSTRIAL USES OF LIME

Richard Givens – Tarmac Lime

Lime, in the form of calcium oxide (quicklime) and calcium hydroxide (slaked or hydrated lime) is probably the earliest "industrial" chemical product known to mankind, and has been used for thousands of years. At first it was likely as a binder in building applications, with some evidence that this was taking place as long as 14000 years ago and as time went on more and more useful properties were discovered – accidentally or otherwise – for this most versatile of materials. Lime is known to have been used in leather tanning in ancient Egypt and in the construction of pyramids and tombs, as a base for decorative finishes in Greek and Roman civilisations, and of course as a building material, with lime stabilised materials incorporated in the Great Wall of China, along with lime mortars and plasters throughout the Mediterranean and beyond. The Romans famously used concrete composed of lime and siliceous volcanic ash with stone and pottery aggregate, to achieve greater strengths more quickly and enable ambitious structures to be built.

Various other applications of lime continued or emerged, from the use in leather tanning to fruit preservation, soil improvement and sanitisation – all of which are still current today, alongside a host of other applications which developed with the explosion of science, industry and technology from around the 17th century.

Today, lime remains an essential component in a huge variety of products and processes which are important parts of our modern society.

SHEQ CULTURE CHANGE AT SINGLETON BIRCH

Axl Farr – University of Hull/Singleton Birch

Singleton Birch Limited has a vision of operating the greenest, cleanest and safest lime works. The company has a lot of tools in place ranging from the Notify incident reporting system to departmental safety representatives. However, even with the introduction of all these systems and procedures, the health and safety performance has somewhat plateaued. A different approach will now be used to re-focus the safety culture.

This project is centred around human factors, why humans act the way they do with each other and the plant. Using human factors methodology, through the exploration stage the safety, health, environment and quality (SHEQ) culture at the company will be assessed, initially through interviews. Various levels of staff from different branches will be interviewed, and the data collected from these interviews will be used to develop a survey. This survey will be distributed to everyone within the company, to assess the culture of the whole site. From this assessment of the company culture, using

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the human factors methodology experience of the knowledge base, a strategy for change will be developed and implemented. The aim is to understand why people act the way they do and change that to improve the SHEQ performance so helping to achieve that vision of operating the greenest, cleanest and safest lime works.

ASSESSMENT OF HYDRATED LIME Ca(OH)$_2$ AS A FAECAL SLUDGE SANITATION TOOL FOR EMERGENCY SETTINGS (CHOLERA TREATMENT CENTRES, REFUGEE CAMPS…)

Diogo Trajano Gomes da Silva and James Ebdon – University of Brighton

Rapid treatment of faecal sludge (FS) in emergency settings (e.g., cholera treatment centres) is key to preventing the onward spread of disease. Our recent research suggests that hydrated lime (Ca(OH)$_2$) may be more effective than chlorine (Cl) at disinfecting FS, due to the large amount of organic matter present. However, despite these promising findings, humanitarian agencies treating FS with Ca(OH)$_2$ have reported high operational costs. Therefore, further optimization of the Ca(OH)$_2$ disinfection protocol is needed. Current practice at the Cox's Bazar refugee camp (Bangladesh) involves the use of 16-20 g/L of Ca(OH)$_2$ to treat FS. The study reported here aims to assess the efficacy of various concentrations of Ca(OH)$_2$ at disinfecting FS. A simulated sludge matrix consisting of dried FS (20%) and raw municipal wastewater (80%) was treated with 16 g/L, 30 g/L, 45g/L, 90 g/L and 135 g/L of Ca(OH)$_2$. Indicator organisms (Total coliforms, E. coli, Vibrio furnissii and somatic coliphages) were used to determine treatment efficacy following contact times of 1hr and one week. Preliminary results showed overall average log reductions (for all indicators) after 1hr and one week as 0.6 and 1.90 (at 16g/L); 1.1 and 4.7 (at 30g/L); 2.4 and 5.3 (at 45g/L); 3.3 and 5.2 (at 90g/L); and 3.3 and 5.1 (at 135g/L), respectively. Initial results suggest that increasing lime dosage from what is currently prescribed, would further improve treatment efficacy. However, further research is underway to establish an optimum concentration which achieves a high log reduction but that does not increase operational costs excessively.

Contact details for presenters at the British Lime Association UK-Lime Research Symposium 2021

To contact any speakers not tabulated here, please contact the British Lime Association: *bla@mineralproducts.org*

Name	Institution	Presentation Title	Contact Information
Dr Giovanni Pesce	University of Northumbria	The importance of academic and industry collaboration in a rapidly changing world	*giovanni.pesce@northumbria.ac.uk www.northumbria.ac.uk/about-us/our-staff/p/ giovanni-pesce/*
Dr Helen Bailey	Driven Company	Hydrated lime in asphalt for longer life roads	*www.driven.co.com*
Olivia Hawrot	Heriot Watt University	Can lime be used to reverse climate change?	*okh2@hw.ac.uk*
Dr Humbul Suleman	Teesside University	The path to decarbonisation for the lime industry	*H.Suleman@tees.ac.uk*
Dr Raffaele Vinai	University of Exeter	Lime from biogenic calcium carbonate for the production of slag-based alkali activated binder	*r.vinai@exeter.ac.uk*
Theodore Hanein	University of Sheffield	Production of slaked lime from limestone at atmospheric conditions and without the release of chemical CO_2	*t.hanein@sheffield.ac.uk https://www.sheffield.ac.uk/materials/people/ research-staff/theodore-hanein*
Tom Cutler	University of Newcastle	Investigating the feasibility of carbon capture options for the lime industry	*www.ncl.ac.uk/engineering/research/civil-engineering/environmental-engineering/*
Angela Rolfe	Ulster University	Technical and Environmental Analysis of Calcium Looping Carbon Capture for Rotary Kiln Lime Plants	*a.rolfe@ulster.ac.uk act-anica.eu*
Carter Newbury	Nottingham Trent University	Site relevant risk of sulphate swell in lime stabilisation	*c/o Dr Paul Beetham*
Dr Richard J. Ball	University of Bath	Lime for mortars and renders	*https://researchportal.bath.ac.uk/en/persons/ richard-ball*
Tugce Busra Su-Cadirci	University of Bath	Importance of mortar substrate interactions in lime masonry structures	*tbs31@bath.ac.uk*
Dr Paul Beetham	Nottingham Trent University	Lime stabilisation in major construction projects	*paul.beetham@ntu.ac.uk*
Rebecca Paramor & Emily McGrath	Nottingham Trent University	Influence of test set up on sulphate swell measurements	*c/o Dr Paul Beetham*
Didier Lesueur	IMT Nord Europe	Hydrated lime in asphalt - Results from recent French sections	*didier.lesueur@imt-nord-europe.fr*
Lindsay Duncan & Elizabeth Graham	University College London	Lime in Precolumbian Construction: Waste and Impact	*https://www.ucl.ac.uk/archaeology/people/ elizabeth-graham-professor-mesoamerican-archaeology www.lamanai.org.uk e.graham@ucl.ac.uk*
Diogo Trajano Gomes da Silva	University of Brighton	Assessment of hydrated lime $Ca(OH)_2$ as a faecal sludge sanitation tool for emergency settings (cholera treatment centres, refugee camps…)	*dds12@brighton.ac.uk research.brighton.ac.uk/en/persons/diogo-gomes-da-silva*

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