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A simple laboratory method to simulate calcite-bonded loose-structured soil samples for collapsibility study

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Abstract

Calcite is one of the commonest bond elements in natural collapsible soils. Where calcite occurs in significant amounts, the soils are considered calcareous. Collapsible soils are characterised by high porosity, high-void ratio, and low-dry density, with the soil particles held together in a honeycomb structure by a bonding agent like clay, suction or calcite. Collapse usually occurs when the bonding agent is lost through wetting, dissolution and/or stressing. Thus, understanding the behaviour of a bonding agent in the collapse phenomenon is critical to design safe and economic foundations built on collapsible soils. For a better interpretation, laboratory-simulated soils have the advantage to ensure controlled soil properties and somewhat homogeneity as against natural soils. Unfortunately, there is no standardized procedure for simulating calcite-bonded collapsible soils. A novel reaction setup developed in-house has been adopted to precipitate calcite bonding through lime gassing. Samples of silt-clay-lime mixes of differing proportions were prepared into varying dry densities to achieve collapsible soil features, and then, CO₂ was passed through the mixes placed in the reaction setup. Gassing was done for 24 h. Samples were labelled A1, A2, A3, B1, B2, B3, C1, C2 and C3, where A, B and C represented silt/clay initial proportioning of 50/50, 35/65 and 20/80, respectively, while 1, 2 and 3 represented lime contents of approximately 9, 20 and 33%, respectively. After gassing, three different methods (*acid–base colour indicator*, *calculated mass gain (CMG)*, and *experimental determination of CaCO₃ content*) were used to confirm the presence or content of CaCO₃ precipitate. Results revealed high levels of successes in terms of lime conversion to calcite and relative homogeneity of samples with collapsible features.

Keywords: Collapsible soils, Calcite bonding, Lime conversion, Gasing, Laboratory soil

Introduction

Calcite (CaCO₃) is a common soil mineral [39] that develops and cements particles enabling soil to maintain a loose structure (Coop and Airey, 2003 cited in Mitchell and Soga [39]). Although other elements like clay and suction also provide support for loose-structured (metastable) soils, in natural collapsible soils, calcite is identified as the main element supporting a metastable structure that collapses upon wetting and/or loading

(Guo, 1958 cited in Li et al. [31], Mansour et al. [34], Milodowski et al. [38], Opukumo et al. [44]).

Apart from degree of saturation or suction, the literature identifies low-dry density, high-void ratio and porosity as common features of collapsible soils [4, 6, 30, 47] and these have been used to fix thresholds to classify collapsibility of soils. For example, in 1958, Clevenger suggested greater than 1.44 Mg/m^3 and less than 1.28 Mg/m^3 as marked dry density thresholds for small and large collapse potentials, respectively [2]. Porosity greater than 40%, silt content greater than 30% are some other reported thresholds for collapse to occur (see [43]). Although clay content was also considered to classify collapse potential (Handy, 1973 cited in Bell and Culshaw [9], Bell et al. [8], Langroudi [29], Okwedadi et al. [43]), unfortunately, other bond materials (e.g., calcite) content or strength have never been considered despite the critical role of bonding on the collapse phenomenon. The second part of this research (to be published) has revealed a relationship existing between bond (calcite) content and compressive strength and collapsibility.

Many loose structured soils supported by calcite of varying proportions occur globally and are sometimes described as calcareous [44]. For instance, the commonly studied collapsible loose structured soils typically referred to as loess covering about 10% of the earth's landmass (from Western Europe to China, across North America and in regions across South America as well as localized areas) generally contain 1–30% CaCO_3 content [25, 31]. In China, loess covers over $630,000 \text{ km}^2$, of which about 60% is loose-structured or collapsible [17]. In Egypt, about 65% of the land is covered by calcareous loessial soils that contain 21–30% CaCO_3 [19]. The main loess deposits of Northern France contain up to 18% CaCO_3 [15]. In the UK, sections of the loose-structured brickearth deposits of south Essex and Kent have been reported to contain maximum of 15.4% CaCO_3 [9, 26, 38]. In Italy, several loose-structured clay soils including the popular Pisa Clay (of the Leaning Tower of Pisa) are also known to contain CaCO_3 contents ranging from 5–100% [23].

Loose-structured deposits are of geotechnical engineering concern as they cause threat to civil infrastructure, lives and economy [44]. For a geotechnical engineer to be able to prevent losses resulting from collapsible soils, one critical aspect is to understand the impact of the loss of interparticle bond on the collapse phenomenon. Despite calcite been one of the main interparticle bonding materials for such loose-structured soils, only a handful researches have attempted laboratory production of controlled calcite-bonded (calcareous) soils for collapsibility studies. For instance, references were cited in Li et al. [31] to have created artificial structural calcareous loess by mixing different proportions of quicklime with natural loess and then adding water and carbon dioxide to produce CaCO_3 bonding. Yet, they presented little or no experimental data or details of procedures, for reproducibility. Therefore, a rigorous study has been conducted here to create novel procedures for effectively manufacturing calcite-bonded soils exhibiting collapsible features.

The study of laboratory-controlled samples is important as they allow targeted properties, e.g., degree of calcareousness and dry density, to be accurately controlled [3], thus providing a clearer understanding of the factors influencing collapse. On the contrary, the inherent variations in natural calcareous soils and the difficulty in recovering undisturbed samples from field pose difficulties in understanding them [3]. However,

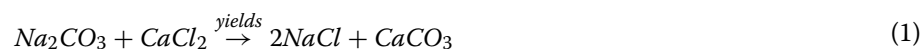
despite the scarcity of procedures for the laboratory simulation of these in the soil collapse theme, there are approaches reported in literature for simulating natural carbonate cementation for other engineering and non-engineering studies (e.g., [1, 3, 5, 10, 18, 21, 35, 36, 40–42, 49, 51, 52]). Some of these works have been adapted in the present study through novel lab procedures (details presented in [Design and production of collapsible samples](#) section) to produce controlled loose-structured (collapsible) calcareous samples.

Methods/experimental

Bringing together knowledge of the two components of this theme, that is, the main physical features of collapsible soils, and available techniques for artificially precipitating calcite, a methodological framework (Fig. S1 in Supplementary Materials) was created to manufacture loose-structured calcareous silty clay samples.

Development of a CaCO_3 precipitation technique

A rigorous process of experimenting some available chemical techniques under lab conditions, to mimic the natural processes of precipitating inorganic CaCO_3 into soils was carried out as part of sets of preliminary studies. Three chemical reaction routes (Eqs. 1, 2, 3, and 4) [1, 5, 18, 41, 42, 49, 52] involving calcium-rich (CaO , Ca(OH)_2 , CaCl_2) and carbonate-rich (Na_2CO_3 , CO_2) compounds were tried under an improvised experimental setup that was progressively modified to fit the purpose. At the end of the preliminary studies, hydrated lime (Ca(OH)_2) reacting with carbon dioxide (CO_2) was adjudged most safe and effective for precipitating solely CaCO_3 , as the other forms of reaction routes were observed to further precipitate unwanted components, such as NaCl and NaOH , which are capable of influencing the mechanical behaviour of samples.



The final reaction setup developed in-house and utilized for the manufacture of the calcite bonded soil samples is shown as Fig. 1. It was developed from a pressure cell with the cell modified to include the following features:

- A gas inlet and an outlet. The inlet allows for CO_2 admittance into cell loaded with the soil-lime compact while the outlet allowed escape of free air from the cell at the early reaction stage.
- Stacking rack. This was used to hold several soil-lime mix prepared either into oedometer test specimens or as large samples. It increases the capacity of the cell to hold a greater number of specimens for each reaction cycle.

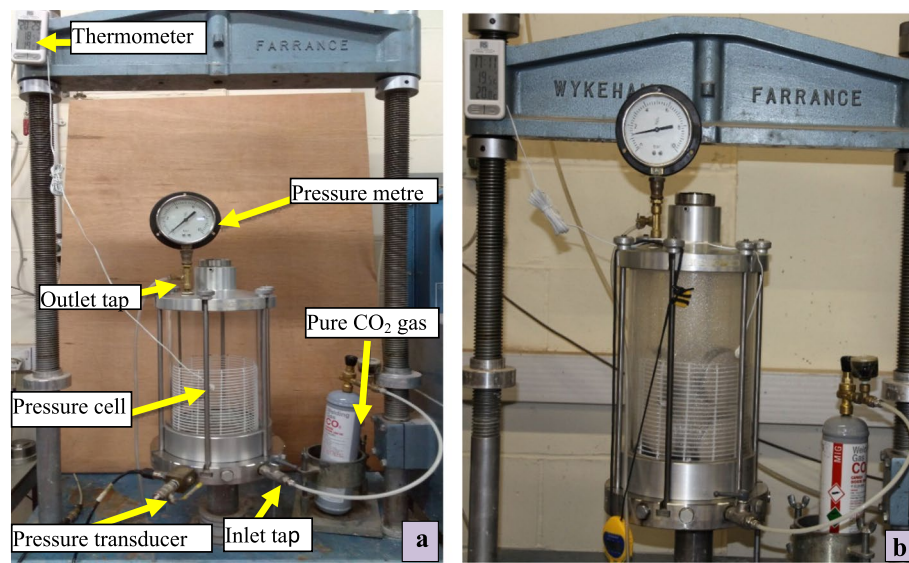


Fig. 1 Reaction apparatus for sample carbonation **a**, empty setup **b**, stacked with oedometric specimens

- Pressure gauges. One fitted to the cell was for closely monitoring both cell pressure and CO_2 capture. The second one was a pressure transducer connected to a computer to monitor rate of CO_2 capture in real-time. This was only employed at the preliminary stage to understand at what time CO_2 capture ceased or became insignificant.
- Thermometer. This was used to measure temperature rise during the carbonation process. Because the thermometer could only read temperatures on the outer pressure cell, the readings were not considered reasonably accurate. If not for time constrain the setup could have been modified to fit thermometer inside cell.

The setup was calibrated by admitting gas into cell up to a cell pressure of about 3 bars, leaving all valves closed and allowing it to stand for up to 48 h. The pressure gauge was observed to deflect only slightly after this period. To remove free air from pressure cell, lime slurry bubbling was adopted. The free air was released (bubbled) into a lime slurry, and the slurry becomes milky and thickens when CO_2 starts bubbling into it. This was observed to begin within the first minute. The escape of CO_2 gas was believed to follow that of free air in the cell because air is lighter and should float on CO_2 gas. The reason for this test was to maintain the high concentration of the CO_2 in the reaction cell.

Key benefits of the above setup include the following:

- The apparatus could confine and distribute gas within cell to virtually all possible reaction fronts in the soil-lime system. Therefore, even carbonation can be achieved.
- Since the pressure distribution is uniform on all surfaces of samples (rather than being fed from one end of the sample), there is a reduced tendency for the gas to cause mechanical damage to the samples (i.e., creation of weak zones or vents).
- Wastage of CO_2 is minimized because only an approximately enough is admitted into the cell while its outlet valve remained closed. The pressure dial gauge deflection indicates CO_2 capture and becomes almost stationary when capturing is nearly com-

plete. A rapid drop in pressure is noticed during the early periods of CO_2 admittance, which gradually slows down. This informs how much more gas should be allowed in the cell enough for a probable complete carbonation.

Confirmation of calcium carbonate precipitate

Before proceeding to carry out a quantitative test to determine the amount of CaCO_3 precipitate post-carbonation and drying, two qualitative methods ((1) and (2) below) were adopted to confirm the presence or otherwise of CaCO_3 in the samples. Leco experimental technique ((3) below) was used for quantitative analysis. Additionally, thermogravimetric analysis and X-ray diffraction were conducted.

- (1) *Acid–base colour indicator*: phenolphthalein turns colourless in near neutral (pH < 8.2) or acidic solutions. At pH approximately 8.2, it begins to show light pinkish colour and progressively deeper colour with increasing pH up to about 9.8 where deep pink emerges. Phenolphthalein solution has been used by many to detect carbonation of lime–treated soils and lime–mortars by spraying it on their fresh broken surface. Where surface indicated deep pink, it shows untransformed portlandite (pH ~12.4) implying no carbonation took place, whereas light pink to colourless indicated different carbonation degrees [5, 18]. CaCO_3 has a pH between 8.0 and 8.5 [5]. The initial soil- $\text{Ca}(\text{OH})_2$ mix before reacting with CO_2 was sprayed with phenolphthalein, and it indicated very bright/deep pink-red colour. Just after reaction, samples were halved, and phenolphthalein solution was sprayed on the inside surface. Non-carbonated portions of the sample showed bright pinkish-red colour while carbonated portions maintained original sample colour.
- (2) *Calculated mass gain (CMG)*. Dry mass of sample pre- and post-carbonation were determined. The difference was compared to an expected theoretical yield. The theoretical change in mass expected was determined as follows: since the molar masses of $\text{Ca}(\text{OH})_2$ and CaCO_3 are 74.09 and 100.09 grams, respectively, in principle, 1 g of $\text{Ca}(\text{OH})_2$ completely carbonated (by CO_2) was expected to be converted to CaCO_3 in the ratio of 1:1.35, representing a 35% increase in mass. This reveals in semi-quantitative terms the amount of CaCO_3 produced.
- (3) *Experimental determination of CaCO_3 content*. The Leco equipment at the Newcastle University Geoscience laboratories was employed to determine CaCO_3 content. Test specimens were obtained from the core of randomly selected samples, and test performed in accordance with BSI7755 [13], Section 3.8, ISO 10694, 1995; Soil Quality, Part 3 (Chemical Methods), determination of organic carbon and total carbon after dry combustion. The total carbon (TC) and organic carbon (OC) were determined, and then, inorganic carbon deduced by difference.

Findings from the development of a CaCO_3 precipitation technique

Consequent upon the preliminary studies, although results not presented here, the following conclusions were reached about the experimental method and some factors

influencing the reaction (which were the guide for the production of the calcite bonded loose-structured samples):

- The durations of reaction, at least those adopted here (6, 12, 24 and 48 h) did not significantly influence the degree of lime-to-calcium carbonate conversion. This agrees with existing knowledge that lime- CO_2 reaction is instantaneous, and the possible delay in this reaction would be reduced accessibility of CO_2 to lime particles.
- Initial reaction moisture content is a major controlling factor for the CO_2 carbonation of lime. Moisture content at a certain threshold (depending on density of sample) appears to favour the reaction. Outside of the threshold carbonation was strongly inhibited, although to a lesser effect below the threshold.
- Observations revealed that at dry state, the reaction was initially delayed before a slow progress was later noticed. It is possible that the CO_2 gas starts condensing due to confining pressure within the reaction cell and thus possibly providing moist conditions that consequently stimulated and gradually progressed the process.
- Though initial dry density appeared to influence the carbonation reaction, it does not in itself affect the process. As the results indicate, samples with similar densities behaved differently following their moisture contents, confirming that the rate and degree of lime-to-calcium carbonate conversion through CO_2 carbonation was mainly diffusion controlled. That is, by the level of CO_2 accessibility to lime fronts. High moisture content in both dense and low-dense compacts resulted in low degrees of lime conversion. This is because CO_2 diffusion in water is very low and access to reaction fronts is rather impeded.
- For effective carbonation, both high- and low-density compacts must contain moisture contents low enough to permit gas access to reaction fronts, and dry carbonation of compacts may not be desired.

Design and production of collapsible samples

Material choices and justification

Studying artificial soil samples can be advantageous because they provide the opportunity both to avoid the inherent variations that occur in natural soils and for target properties to be accurately controlled.

Mixtures of different proportions of a commercial kaolin (see Table S1 in Supplementary Material for details) and an alluvial quartz-silt were prepared and referred to as primary soils. Then, calcite was precipitated (via the carbonation of hydrated lime ($\text{Ca}(\text{OH})_2$) (see Table S2 in Supplementary Material for details) using the innovative setup as previously described) in different amounts into the primary soils to form twelve different samples. Kaolin and quartz-silts were preferred because of (1) their physico-chemical nature. Both kaolin clay and quartz-silt are stable and chemically inert, which means they will not interfere with the chemical reaction required to precipitate CaCO_3 . (2) They form the composition of commonly studied (natural and engineered) collapsible soils, e.g., alluvial silts are typical of loessial soil [15]. Common collapsible soils have grain sizes ranging between clay ($\leq 2 \mu\text{m}$) and silt ($2 \mu\text{m} < 63 \mu\text{m}$) and sand in some cases [4, 6, 16, 34, 47].

Even though some of the key criteria for collapse, e.g., low-dry density, high-void ratio and porosity have been deliberately exaggerated ($\sim 1 \pm 0.1 \text{ Mg/m}^3$, 1.1–1.8, 52–65, respectively) in the studied samples to better understand the bond impact of CaCO_3 on the collapse phenomenon, values are however comparable to soils studied by the authors such as Hull [20], Allman and Poulos [3], Ismail et al. [22]. Furthermore, normally consolidated clay have void ratio, e and porosity, n of 1.73 – 3.86 and $\sim 60\%$, respectively [28], and natural sediments have $e = 1.0\text{--}6.0$ and $n = 50\%$ [48]. Sterianos [50] reported void ratio values between 1 and 2 as typical of natural carbonate sediments. These values compare to those of the present samples. Also see Bui et al. [14] for more global void ratios and porosities.

Following researchers, e.g., Lawton et al. [30], Basma and Tuncer [7], Assallay [4], Medero et al. [37], Jefferson and Ahmad [24], who produced (non-chemically bonded) artificial collapsible soils mainly by compaction (by either volume control or varying compaction moisture contents) to achieve predetermined dry densities, void ratio and saturation, this study has adopted the same methods in conjunction with the CaCO_3 precipitation method examined above, to produce samples. Proportions of CaCO_3 precipitated are similar to those occurring in many natural clays and some loessial soils (see [15, 19, 25, 31]).

Sample constitution and production procedures

The flow diagram (Fig. 2) below shows the stages involved in the production of samples. Samples were simply constituted with predetermined material proportions as presented in Table 1. Prior to the calcite precipitation, the index properties of constituted materials (primary soils) were determined (Table S3 in Supplementary Materials).

Details of procedures

- (1) Mix designs presented in Table 1 were chosen for this study. Three soils with clay/silt proportions of 50/50, 65/35 and 80/20 were first created and referred to as primary soils A, B and C, respectively, and their Atterberg limits determined (Table S1 in the Supplementary Material). Each of these primary soils were then mixed with 0, 10, 25 and 50% Ca(OH)_2 (by mass of primary soil) in a dry state for several minutes until a uniform distribution was obtained. This formed twelve samples with constituent proportions as shown in the Table 1. The samples were labelled A0, A1, A2 and A3; B0, B1, B2 and B3; C0, C1, C2 and C3 where 0, 1, 2 and 3 represent the 0%, 9%, 20% and 33% Ca(OH)_2 , respectively. 0% Ca(OH)_2 represented non-calcareous sample while the other values correspond to estimates of CaCO_3 contents expected to precipitate to produce *moderately*, *strongly* and *very-strongly* calcareous samples, respectively. Apart from these main samples, others (named D1, D2 & D3) have also been constituted for certain checks as the project progressed.
- (2) Primary soil- Ca(OH)_2 mixes were tested to obtain their optimum moisture contents (OMC) and maximum dry densities (MDD) (Table S1 and Fig. S2 in Supplementary Material) in accordance with relevant sections of BS1377 [12]. After this, the nine samples containing lime were each prepared to two different moisture contents ($100 \pm 2\%$ of OMC and $50 \pm 2\%$ of OMC) for compaction to vary density

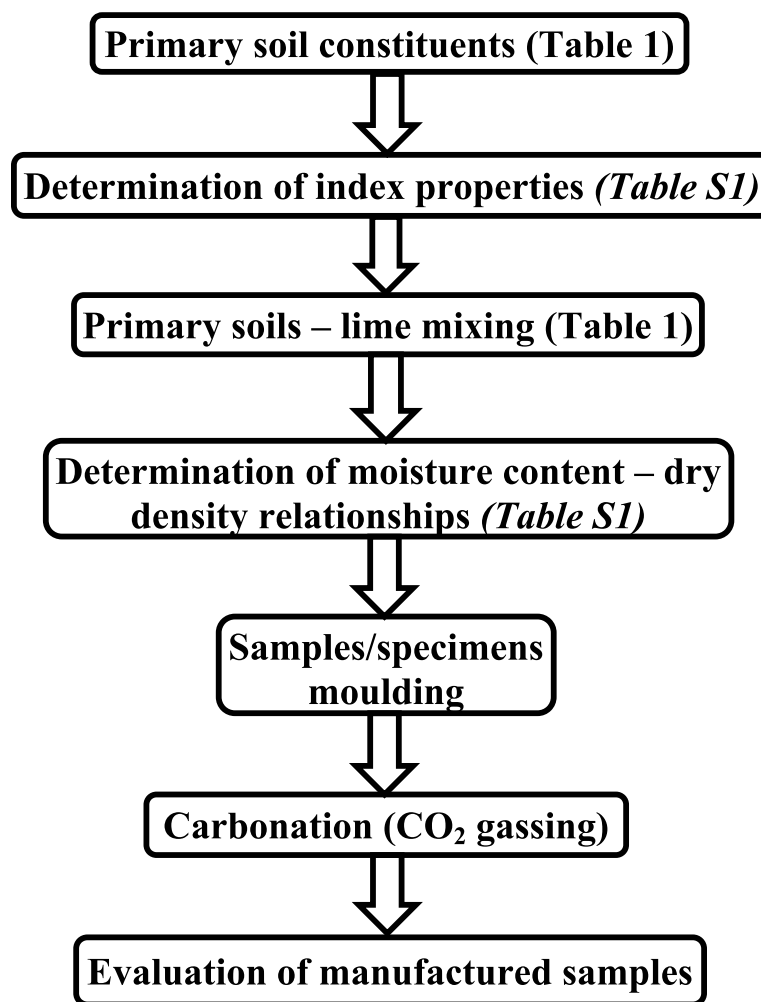


Fig. 2 Summary of samples production procedures

related properties. The soil–Ca(OH)₂ systems were mixed with the appropriate amount of water by thoroughly kneading by hand (with rubber gloves on) to avoid local wetting and the formation of lumps. Kneading continued for several minutes until samples were observed to be smoothly consistent, then stored in air-tight sealable plastic bags for a period not less than 48 h under room temperature for moisture homogenization. Compaction using the standard Proctor (lightweight rammer, 2.5kg) and static (volume-controlled) methods were then adopted to obtain various densities.

- (3) (i) Samples compacted with the standard Proctor method, having a height and diameter of 115 and 105 mm, respectively, were extruded from compaction mould (by means of a hydraulic jack) and divided into approximately four equal parts (to reduce thickness for effective CO₂ penetration) within a short space of time. Cut samples were covered with plastic bags to avoid moisture loss. Samples prepared with water contents higher than approximately 15% were allowed to air dry until moisture contents fell to or below that level (based on preliminary results) before proceeding to the carbonation stage. On the other hand, those samples mixed with

Table 1 Designed soil sample composition: degree of calcareousness defined according to Day's 1983 classification of calcareous soils, cited in Kishchuk [27]

Sample	Composition				Theoretical expected after carbonation	
	Before carbonation					
	% Silt (quartz)	% Clay (kaolin)	Clay/silt ratio	% Ca(OH) ₂	% CaCO ₃	Calcareousness
A0	50	50	1	0	0	None
B0	35	65	1.9	0	0	None
C0	20	80	4	0	0	None
A1	45	45	1	9	~ 12%	Moderately
B1	31	59	1.9	9	~ 12%	Moderately
C1	18	72	4	9	~ 12%	Moderately
A2	40	40	1	20	~ 25%	Strongly
B2	28	52	1.9	20	~ 25%	Strongly
C2	16	64	4	20	~ 25%	Strongly
A3	33	33	1	33	~ 40%	Very strongly
B3	23	43	1.9	33	~ 40%	Very strongly
C3	13	53	4	33	~ 40%	Very strongly

water contents lower than this were taken for carbonation immediately after compaction and cutting.

- (ii) For statically compacted specimens, only samples mixed with $50 \pm 2\%$ of OMC were used to prepare specimens to predetermined dry densities. Oedometric and compression test (CT) specimens were prepared using respective split moulds. These moulds, with known volumes, were assembled with their bases and appropriate amounts of prepared soil (to achieve predetermined dry densities) were carefully and gradually emptied into the moulds, ensuring even distribution. The top pistons were then placed on top of the soil and then statically compacted by the aid of a dead load until the gap between the mould and top piston closed completely. Where a dead load could not fully compact, a loading machine was employed. At full closure of the top piston, compacted specimens were left a few minutes before removing the load and disassembling the mould to avoid possible rebound of the soil. The oedometric specimens were compacted into an oedometer ring assembled into the compaction mould while CT specimens were compacted directly into the moulds. Both specimens were retrieved by splitting the moulds. However, in some cases, CT specimens were better retrieved by extrusion using a hydraulic jack. Moulded specimens were then weighed and transferred into the carbonation cell.
- (4) Carbonation of the compacted samples/specimens following the procedures noted in earlier. The preliminary study indicated that any time between 6 and 48 h enough for the carbonation required. Thus, 24 h was chosen for convenience.
- (5) Wet carbonated samples/specimens were weighed immediately upon removal from the carbonation cell and then oven dried (temperatures between 45 and 50°C) to obtain dry or unsaturated conditions.
- (6) The success of the reaction process, in terms of degree of lime conversion, was also evaluated following methods (2) and (3) stated in [Sample constitution and produc-](#)

tion procedures section in addition to thermogravimetric analysis and X-ray diffraction (XRD). Scanning electron microscopic (SEM) images were also obtained to examine the microstructure of the manufactured specimens in comparison with collapsible soils in the literature. Specimens used here were oven dried at standard temperatures (between 110 to 115°C), which revealed moisture contents ranging from 0.12 to 0.45% retained after the first oven (45–50°C) drying. This would likely cause some form of discrepancies in the “calculated mass gain” evaluation method.

Results and discussion

Determination of amount of CaCO_3 precipitate and evaluation of degree of success

The procedures for the calculated mass gain (CMG) and Leco experimental yield (LEY) methods have been earlier examined. Another experimental technique used to quantify CaCO_3 precipitate was the thermogravimetric analysis (TGA) whose results are herein referred thermogravimetric experimental yield (TGAEY). Summary of signatures of the TGA are presented as Figs. S3 and S4 in Supplementary Materials for *sample series A* and *C*, respectively. The experiment was a simultaneous thermal analysis (STA) of thermogravimetry and diffraction scanning calorimetry (TG/DSC).

The results obtained from all three methods are compared between methods as well as with theoretically expected yield (TeY) in Fig. 3 below.

The CMG results plotted in the Fig. 3 represent average of 8 specimens for each sample and revealed carbonation successes in the ranges shown in Table 2. The experimental yields (EYs) on the other hand were determined in each case with a representative specimen chosen at random. A summary of approximate degrees of carbonation from both experimental methods are also shown in the Table 2 including some undiscussed collapse potential (CP) results obtained from a one-dimensional oedometer test at 300 kPa wetting stress. A full study on CP is to be published separately.

Results of the lime-to-carbonate conversion levels evaluated by the three different methods show close comparisons between methods in many cases but differ quite significantly in a few others possibly due to systematic error. However, on a general note, adequate carbonation of approximately 90% were achieved. As can be seen in all plots in Fig. 3, CMG appear to match closer with the TeY than the experimental methods. Nevertheless, in the samples with low-initial lime contents (9 and 20%), CMGs are comparable to the experimental yields (EYs) with variations not more than 2% CaCO_3 content. However, in samples with high-initial lime contents (33%), variations reaching about 5% were observed.

Apart from experimental errors, these variations between methods could happen due to several factors. For instance, loss of particles during handling and incomplete drying would, to some extent, undermine the CMG results. On the other hand, metal oxides other than calcium oxides inherent in samples constituent materials could react with CO_2 to form carbonates heavier than CaCO_3 , giving mass gains different from that resulting from lime conversion. Consequently, more credence has been accorded the EY data (experimentally obtained) in the following discussion.

As expected, more Ca(OH)_2 reacted produced more CaCO_3 . This is not surprising since in all reaction cases sufficient pure CO_2 was available to be absorbed by all existing

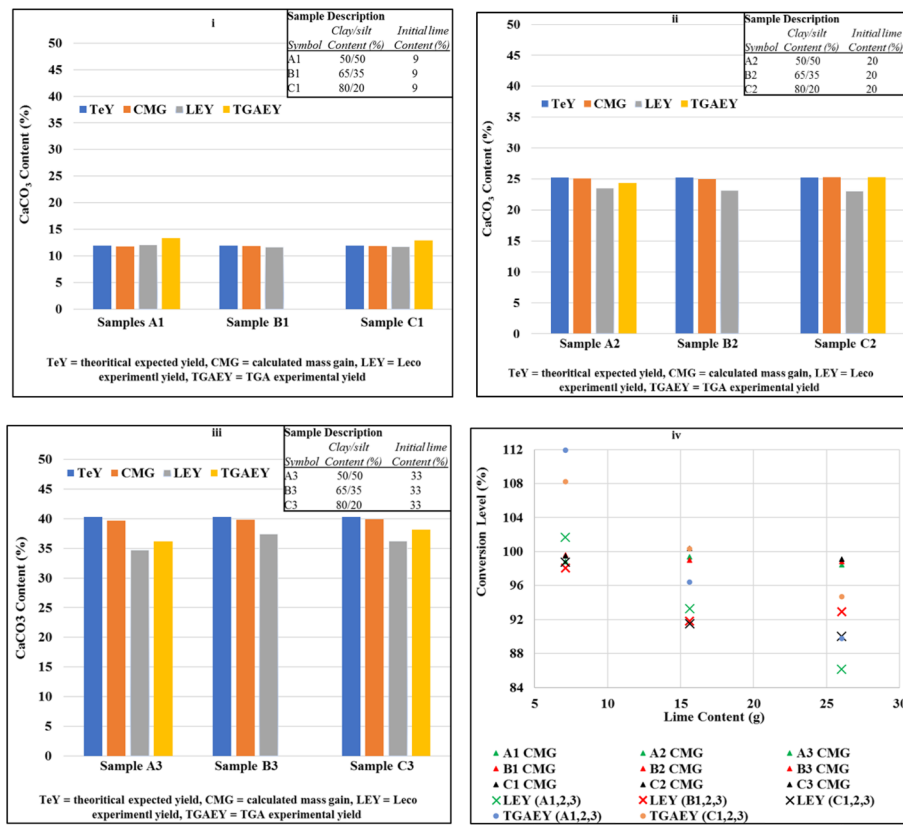


Fig. 3 Carbonation success level as related to the theoretical expected CaCO_3 yield (i) moderately calcareous (ii) strongly calcareous (iii) very strongly calcareous samples (iv) percent lime-to-calcium carbonate conversion levels

Table 2 Summary of the degree of lime-to-carbonation conversion as evaluated by the different methods, plus collapse potential values of manufactured samples

Degree of lime-to-calcium carbonate conversion (%)				Collapse potential (%)
Sample	Calculated mass gain (CMG)	Experimental yield (EY) Leco yield (LEY)	TGA yield (TGAey)	
A1	99±1.5	101.7	111.9	20.2±0.33
A2	99±0.3	93.3	96.4	1.3±0.09
A3	98±0.3	86.2	89.8	0.2±0.04
B1	100±0.7	98.1	-	18.8±0.49
B2	99±0.7	91.8	-	0.8±0.17
B3	99±0.3	92.9	-	0.1±0.14
C1	99±0.9	98.7	108.2	17.0±0.19
C2	100±0.5	91.5	100.3	0.4±0.01
C3	99±0.2	89.9	94.7	0.1±0.02

lime particles. However, carbonation (or conversion) levels achieved were rather of the contrary. Lower degrees of conversion with increasing initial lime contents were almost a general trend but more evident in the EY results. $\text{Ca}(\text{OH})_2$ -to- CaCO_3 conversion

levels recorded for the nine samples range between 86 and 112% as indicated in Fig. 3iv. While it remains unclear why conversion levels (though in limited cases) may exceed 100% (possibly, due to systematic error), there are possible explanations as to why lesser conversion levels have been achieved, especially those with higher initial lime contents. Perhaps, yields in excess of 100% of the expected are the result of carbonate precipitates other than CaCO_3 , which the experimental techniques could not distinguish.

Early carbonation can result into CO_2 flow restrictions. Since hydrated lime (particle density 2.24g/m, molar volume 33.01) increases in volume by $\sim 11.8\%$ when carbonated [40], it is understandable that higher lime content in a compacted sample will bring greater volume of expansions filling the internal pore spaces. Thus, CO_2 accessibility to other potential reaction fronts could be limited bringing about slower carbonation rates at later stages of the reaction process. Despite that this trend was noticed only in the EY data, another reason for this occurrence can be explained from the perspective of energy yield. Because a mole of Ca(OH)_2 reacted with CO_2 yields about 74 KJ heat energy [40], the carbonation reaction can be impacted by heat energy in the following ways: (1) increased temperature reduces CO_2 density, potentially reducing its diffusion in water and (2) high temperatures accelerate moisture loss and can cause moisture starvation needed to proceed the carbonation reaction. It has been observed in the present study that heat generated during the carbonation process increased with increasing amount of lime reacted. From this understanding, it is possible that higher heat energies generated in higher lime compacts might have caused evaporation of both the catalysing moisture as well as those generated during the process, leaving some lime particles in the compact devoid of moisture needed to progress the reaction.

An interesting situation regarding moisture was observed during the carbonation period. Surprisingly, samples with higher lime contents having higher pre-carbonation moisture contents, retained lower moistures after carbonation as shown in Fig. 4. Since water is one of the yields from this reaction, it was expected that moisture generation would increase with increasing lime content. This appeared so but only for the water that condensed on the reaction cell. It may imply, therefore that the excess heat generated resulted in higher evaporations leaving samples dryer.

Again, the higher heat energies, according to Moorehead [40] could have reduced the CO_2 solubility in water, delaying the reaction. However, this will be insignificant for temperatures up to 90°C [10, 49, 51, 52]. As noted previously, CO_2 solubility is critical to produce CO_3^- ions, which will react with dissolved Ca^{++} to form CaCO_3 .

Van Balen [51] also considered surface passivation of lime particles at early carbonation as a possible condition that could prevent CO_2 from reaching particles cores, resulting in reduced conversion levels. Conversely, Vance et al. [52] are of the opinion that early carbonation and surface volume expansion should result in surface exfoliation of the early formed CaCO_3 and coupled with the nonuniform morphological structure and irregular growth of calcite, more vents should develop allowing for greater CO_2 penetration.

The research carried out by Moorehead [40] also highlighted more factors which may be responsible for low carbonation rates with increasing lime content in a compacted soil. These present results agree with most of Moorehead's arguments except that he stated that carbonation levels could only reach a maximum of 90%. However,

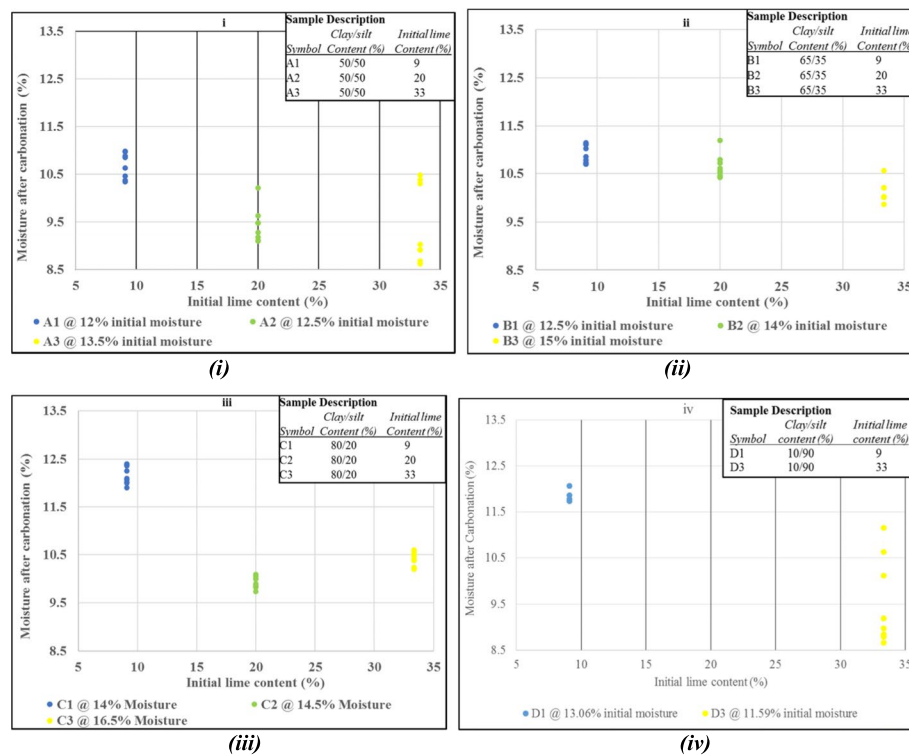


Fig. 4 Relationship between amount of lime carbonated and moisture retained

Freshly prepared clay-lime compact.

Compact after few minutes of carbonation



Fig. 5 Carbonation progressing from compact surface towards core

he used a quite simple compacted material, that is, pure glass particles and lime. Again, Moorehead's samples carbonated for a maximum of 60 min while 24 h was adopted here. While lime carbonation reaction may be considered instantaneous, 60 min may be insufficient time because the carbonation process of a lime sample progresses from surface to core (see Fig. 5), and therefore, the rate and duration to achieve complete carbonation will depend on the physical conditions of the sample.

It is recommended that further research be carried out to identify reasons for excessive mass gain as found in this study. Nonetheless, it is worth noting (from the material data sheet) that the hydrated lime carbonated herein consisted of about 3–5% other metal compounds and oxides, such as magnesium hydroxide ($\text{Mg}(\text{OH})_2$), iron

oxide (Fe_2O_3), alumina (Al_2O_3), Lead (Pb), and Manganese (Mn), which can react with CO_2 to possibly form other minor carbonates heavier than CaCO_3 .

As evident in Fig. 3, in general, results of both assessment methods do not differ considerably with the theoretical one, which is an indication of nearly pure carbonate samples.

X-Ray diffraction (XRD) analysis

A powder X-ray diffractometer, PANalytical X'pert Pro Multipurpose Diffractometer, powered by a Philips PW3040/60 X-ray generator fitted with an X'Celerator detector was used to examine samples. Phase identification was performed by means of the X'Pert accompanying software, PANalytical High Score Plus in conjunction with the ICDD Powder Diffraction File 2 Database (2004), ICDD Powder Diffraction File 4 - Minerals (2018), the American Mineralogist Crystal Structure Database (2010) and the Crystallography Open Database (2016. www.crystallography.net).

XRD analyses were performed on both non-carbonated and carbonated samples to identify the crystalline phases and physical characteristics of their components. Identifying the main phase of the CaCO_3 precipitated from the carbonation process was one of the objectives of this study. Crystalline CaCO_3 is known to exist in three polymorphs (calcite, aragonite or vaterite) with varying chemical stabilities. Calcite being the most stable and vaterite the least stable. Mineral phase or crystal structure controls the pattern of X-ray diffraction obtainable, and almost all crystalline solid materials possess a unique powder X-ray diffraction form in terms of the peak intensities and the positions of the observed reflections [53], which aid their identification when compared to X-ray databases. Usually, their X-ray spectra show strongest diffraction peaks at their unique angles (degrees, 2 theta). Stronger diffraction peaks also indicate dominance of a mineral in a sample. Some diffraction peaks defined in literature (Table S4 in Supplementary Materials) are adapted to evaluate those obtained in this present study (Figs. 6 and 7).

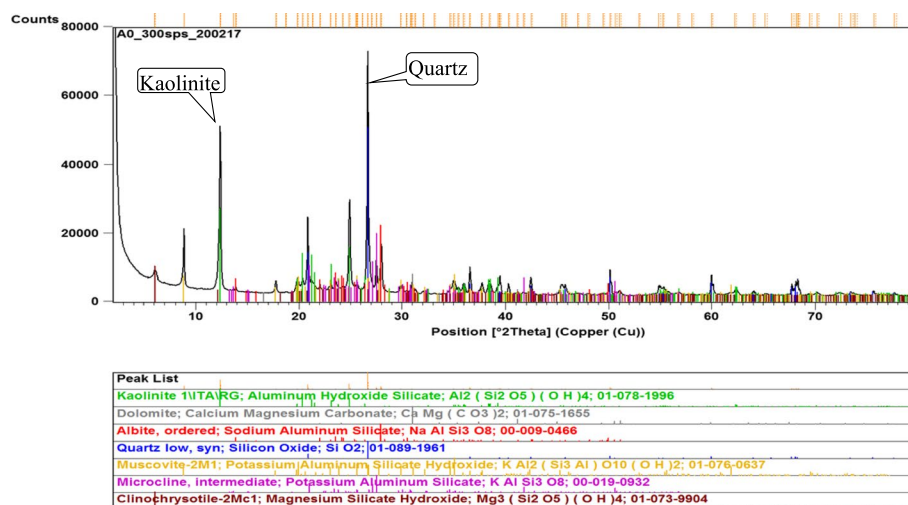


Fig. 6 Typical mineral composition of initial samples without lime/carbonate treatment, identified by X-ray diffraction analysis

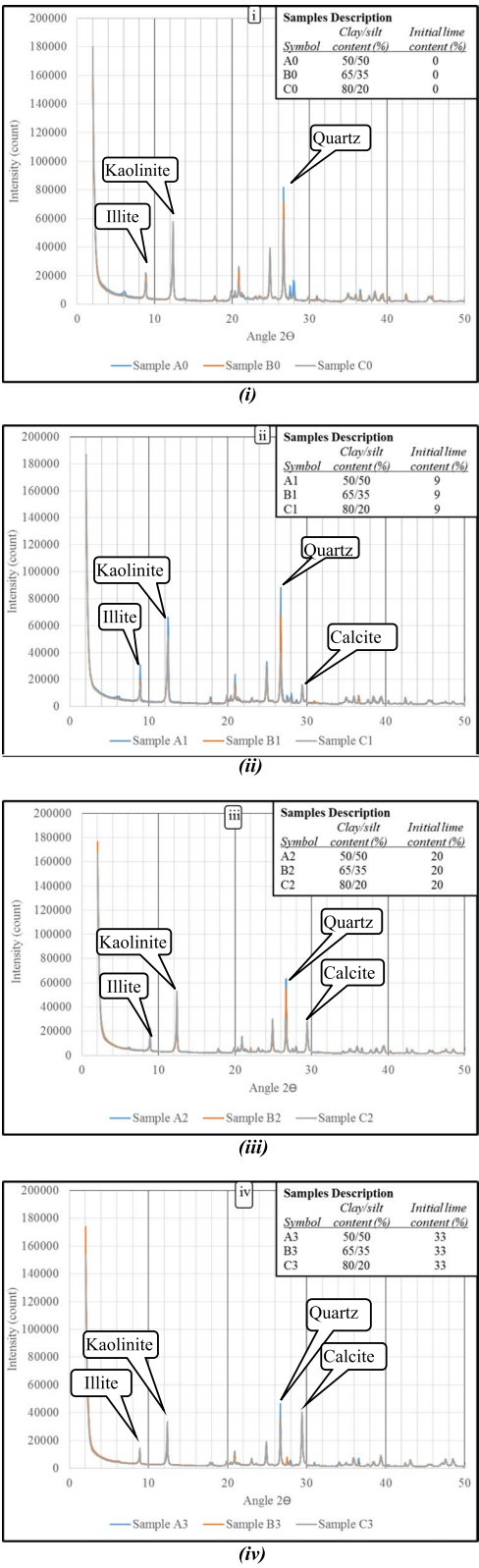


Fig. 7 X-Ray diffraction analysis of manufactured samples (i) initially constituted primary soils, (ii) moderately calcareous, (iii) strongly calcareous and (iv) very strongly calcareous samples

Figure 6 shows the typical initial mineral constituents of samples before lime or calcium carbonate treatment. Here samples were only different from one another in proportions of these minerals. Predominantly, the exercise was to identify and quantify the calcium carbonate phase precipitated from the carbonation process, since other key components of the samples were fairly well known from initial constituent proportions.

All the X-ray diffraction spectra of both initially constituted soils (Fig. 6) and manufactured samples (Fig. 7) show good consistency, an indication of the repeatability of the production method. By comparing diffraction angles identified in Table S4 in Supplementary Material with those of Figs. 6 and 7, it becomes clear that primary soils, i.e., samples before lime/carbonate treatment, were composed mainly of quartz ($26.5^{\circ} 2\theta$) and kaolinite ($12.38^{\circ} 2\theta$) minerals with minor others. Interestingly, all the different manufactured samples revealed that, post carbonation, only calcite ($29.5^{\circ} 2\theta$) was the new mineral introduced. Calcite is the most stable form of CaCO_3 [39].

Micro-fabric analysis

Scanning electron microscope (SEM) images were obtained using a TESCAN VEGA LMU scanning electron microscope to study the micro-fabric of samples. Prior to scanning, specimens were oven dried and mounted on an aluminium stub with Achesons Silver Dag and then dried overnight, followed by gold coating (standard, 15nm), using a Polaron SEM Coating Unit. Then, the SEM images were analysed by digital image processing using PCAS (Particles (Pores) and Cracks Analysis System) to identify and quantify microporosity (Fig. S5 in Supplementary Materials).

PCAS is a professional software developed according to image processing technologies to automatically identify multiscale pores and cracks and has been employed by several researchers (Liu et al. [32, 33] and references therein) in the quantitative analysis of SEM images and photographs of rock and soil cracks, micropores and mineral particles. The software is almost automatic, requiring just two thresholds to be (1) gray-level threshold (80 chosen here) and (2) minimum pore area (50 pixel chosen here). The image is then automatically processed in the software and returns all geometric parameters of the pores and the statistical parameters of the pore system.

As noted earlier, samples manufactured in this study did not mimic a particular soil but rather merely simulate in general terms, an open metastable structure. Despite that, observations of the SEM micrographs reveal similarities in microfabric appearance with some SEM images of natural collapsible soils reported in the literature. This proves the validity of the procedures adopted here.

Regardless of the identical mineralogy of samples, the SEM micrographs show different microfabric from one sample to another. This may be because of differences in proportions of constituent materials, suggesting that the microfabric was basically controlled by the mix design. However, nearly all samples exhibited an open structure (i.e., large porosity), with intergranular pore sizes reducing with increasing clay and carbonate content. Conversely, the PCAS image processing revealed an increase in pore number (porosity) with increasing clay content.

The image processing results depended mainly on discrimination of pores and particles as black and white spots, respectively. This was enhanced by threshold adjustments. To be able to compare processed image results logically, general threshold values were

chosen. However, a major drawback was that of the quality of the original SEM images. For instance, in some cases, soil particles appeared dark on the original SEM image and those were also identified as pores in the PCAS analysis. Notwithstanding these issues, observations by eye revealed that intergranular pore sizes in all of the micrographs are visible measuring in the range of macroporosity (i.e., pores wider than $0.05\mu\text{m}$ [45]).

Whereas other experimental data confirmed the precipitation of calcite in the main samples (A, B and C series) of this project, it was difficult to physically recognise CaCO_3 in the SEM images, in terms of identifying CaCO_3 shapes. However, carbonate globules were suspected in the sample A series. It was concluded that, perhaps because of the high quantity of clay mineral in the samples, it was possible that clay could have overshadowed the systems making carbonate shapes opaque.

Consequently, a silty soil with only about 10% clay was carbonated following identical procedures as with the main samples. In a subsequent SEM analysis, therefore calcium carbonate shapes (globules and needle-like) became visible in samples with high-silt content (that is, samples A and D series) being more conspicuous in the high carbonate ones (A3 and D3). The calcium carbonate can be seen to coat silt particles in sample D3, and carbonate-forming contacts between coated grains while samples of the A series appeared to have both carbonate and clay occurring together as the silt grains coating. Large silt grains appear clean in sample D1. No grain coating was however observed. Rather, silt particles are seen to contact each other in a random manner with what appears to be menisci of calcite and accumulation of globules at the top left corner.

Observations of the SEM images generally show that microfabric of the samples vary from one to another, except in few cases where some similarities were noticed. These variations are perhaps, due to the differences in proportions of constituent materials. Microfabric is one key feature that defines the collapsibility of a soil [11, 46]. As such, the collapse potential (CP) of the present samples may change with change in proportion of soil constituent materials. However, in natural collapsible soils, not only the proportioning of constituent materials but a combination of sedimentation mechanism and grain type influence the structure of metastable soils [47]. These factors determine the packing state, thus, dry density, void ratio and porosity.

Obviously, the samples exhibited a large open structure (see Fig. S5 in Supplementary Material) with estimated void ratios, e above 1.5 and porosities, n_o greater than 60%, satisfying the “> 40%” criterion for collapse to occur according to Fedá, 1966 (cited in Alan and Robert [2]) while the second set of samples exhibited significantly lower e , with n_o still greater than 40%, satisfying the collapse criterion. Each set of samples exhibited higher e and n_o with decreasing calcite and clay contents. However, there has also existed a nominal increase in dry density with higher calcite contents, which might be a result of the mass increase of lime following its transformation.

Conclusions

- The literature concludes that nearly every soil type can potentially be collapsible under the right conditions. The prerequisite for collapse being an open metastable structure, with main soil features including low-dry density, high-void ratio and porosity, enough inter-particle bonding, and unsaturated nature (except quick clays).

- This study concludes that an open metastable structure can be replicated in the laboratory through a controlled process that produces fixed amounts of precipitated calcite as bonding element. This was possible through volume-controlled compaction of lime-clay mixes followed by CO₂ gassing.
- The process of lime conversion to calcite by gassing was found to be instantaneous, but in a lime-clay compact, carbonation through to the core of compact depends on time. Furthermore, carbonation success for such a system is controlled mainly by density, water content and lime content. Certain combinations of dry density and water content hinder the access of CO₂ gas to potential reaction sites whereas, high-lime contents are suspected to bring about the effect of surface passivation.
- The microfabric of manufactured samples can be comparable with that of natural collapsible soils. In the artificial samples, microfabric varies from one sample to another due to differences in proportions of constituent materials. There were no clear trends in this variation, but pore volume was observed to broadly increase with decreasing clay and calcite content.

Abbreviations

BS	British standard
BSI	British Standard Institute
CP	Collapse potential
CMG	Calculated mass gain
CT	Compression test
<i>e</i>	Void ratio
EY	Experimental yield
ISO	International standard organization
LEY	Leco experimental yield
MDD	Maximum dry density
<i>n</i>	Porosity
OC	Organic carbon
OMC	Optimum moisture content
PCAS	Particles (pore) and cracks analysis system
SEM	Scanning electron microscope
STA	Simultaneous thermal analysis
TC	Total carbon
TeY	Theoretically expected yield
TGA	Thermogravimetric analysis
TGAEY	Thermogravimetric experimental yield
TG/DSC	Thermogravimetry and diffraction scanning calorimetry
UK	United Kingdom
XRD	X-ray diffraction

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s44147-022-00114-3>.

Additional file 1: Figure S1. Stages of the methodological framework to produce loose-structured samples. Table S1. Properties of Polwhite E China clay reported by supplier. Table S2. Properties of the hydrated lime as presented by Lafarge Tarmac, 2016. Table S3. Index properties of Primary Soils with varying proportions of lime (uncarbonated). Figure S2. Moisture content – dry density relationship of primary soils with varying lime contents. Table S4. X-Ray diffraction angles of minerals as adapted from the literature. Figure S5. a and b - SEM micrographs of manufactured samples and their microporosity analysis using PCAS. Black areas represent pores in the PCAS images.

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Authors' contributions

This article is part of the PhD work of the first author (Opukumo, Alfred Wilson). The PhD work was jointly supervised by the second (Davie, C. T.) and third (Glendinning, S.) authors at the School of Engineering, Newcastle University, UK. The authors have read and approved the manuscript.

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Availability of data and materials

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

Declarations**Competing interests**

The authors declare that they have no competing interests.

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