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Carbonate binders by ''cold sintering'' of calcium carbonate

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Abstract The solubility of calcium carbonate (limestone) particles depends on the amount of CO_2 dissolved in the water, which is a function of temperature and the pressure of CO_2 that is in equilibrium with water. At a constant temperature, increasing CO_2 pressure increases the solubility of $CaCO_3$, and decreasing CO_2 pressure favours the crystallisation of $CaCO_3$. This dissolution–crystallisation behaviour of $CaCO_3$ can be used in the development of carbonate binders—a process called ''cold sintering''—of limestone. This paper examines the effect of a range of parameters on the cold sintering process of limestone powder. The parameters studied are CO_2 gas pressure (atmospheric, 10 atm and 35 atm), exposure time (0–90 min), post-compaction pressure (10 and 15 MPa) and compact pressing time (10–60 min). The water/limestone powder ratio was kept constant at 0.2 (by weight). The compressive strength of the limestone compacts was used as a measure of the efficiency of the carbonate binder formation process, and scanning electron microscopy was used to study the microstructural developments. The results show that carbonate binders can be produced by cold sintering of limestone powder. Exposure of limestone compacts to high CO_2 pressure followed by post-compaction at high mechanical pressure, enhances the strength of the compact. From the microstructural data, it is evident that newly formed calcium carbonate crystal growths are responsible for the strength improvements observed. The amount of water that is used in the limestone powder mixture is one factor that controls the quantity of the cementing phase. Future work has to be focussed on the application of methods to further increase the solubility of calcium carbonate, as the amount of calcium carbonate available for recrystallisation is important in producing a strong binder.

Introduction

The process of gathering particulate matter into a conglomerate is called agglomeration. The binding mechanisms of the agglomeration can be of several types, and binding via solid bridges is one of them. Solid bridges between particles can occur as a result of sintering, chemical reactions or crystallisation of dissolved substances. In the latter case, the solid bridges between particles are created by a dissolution–crystallisation process at the grain surfaces. The strength of the crystal bridges would depend on the amount of crystallising material and the speed of crystallisation [1].

A process similar to agglomeration by dissolution–crystallisation also occurs in nature, during the diagenesis of sedimentary rocks. A range of factors such as temperature, ionic concentrations and compaction pressure, influence this process. Carbonates are more susceptible to diagenesis, and the dissolution and crystallisation behaviour of carbonates play an important role in this regard [2].

The dissolution and crystallisation behaviour of $CaCO_3$ has been applied and reported in the production of $CaCO_3$ agglomerates in a few studies [3–5] using a technique

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called hydrothermal hot pressing. Hydrothermal hot pressing is a technique by which hard solid bodies of powders can be produced in a short time, at a relatively elevated temperature under saturated vapour pressure. This technique has been used for the solidification of cementitious materials, and can be used for the solidification of thermal decomposable carbonate powders such as $CaCO_3$, $MgCO_3$ and $SrCO_3$. In this method, powder samples are subjected to a high compaction pressure (15–35 MPa) and temperature (40–300°C), followed by a cooling step. In the case of $CaCO_3$, salts such as NaCl and $CaSO_4$ or acetic acid have been used in the mixture to enhance the dissolution of $CaCO_3$. Solid bridges between powder particles are formed due to the dissolution and recrystallisation of $CaCO_3$ in between grains.

It is a known fact that apart from the presence of other salts, the solubility of $CaCO_3$ in water also depends on the dissolved CO_2, the concentration of which is a function of temperature and pressure of CO_2, in equilibrium with water. As CO_2 pressure increases, at a constant temperature, the solubility of $CaCO_3$ increases, and at constant CO_2 pressure, the solubility of $CaCO_3$ decreases with increasing temperature. In water free of CO_2, the solubility of $CaCO_3$ is exceedingly small [6, 7].

Carbon dioxide, when dissolved in water, transforms to carbonic acid. Calcium carbonate dissolves in carbonated water, resulting in Ca^{+2} and HCO_3^{-1} ions, via the following reactions:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{+2} + 2HCO_3^{-1}$$

These reactions are reversible, i.e. the removal of CO_2 from water (by suitable methods) will result in less acidic conditions that favour the reprecipitation of dissolved $CaCO_3$. Depending on the distance between $CaCO_3$ grains, recrystallisation can create solid bridges between particles, resulting in agglomerates of solid $CaCO_3$. This property of $CaCO_3$ can be used in the development of carbonate binders using limestone powder as the raw material. As the agglomeration process can occur at ordinary (low) temperatures, it can be categorised as a ''cold sintering'' method.

In the development of carbonate binders in situ by the cold sintering process of limestone, some factors are to be considered. Mainly, the experimental conditions have to be met that facilitate dissolution, followed by reprecipitation of $CaCO_3$ at or near particle contact points. The amount of $CaCO_3$ reprecipitates and the distance between the grain points play an important role in determining the efficiency of the carbonate binder (solid bridge) formed. The amount of carbonate dissolved will depend on the applied CO_2 pressure, temperature, the amount of water in the compact, and the particle size and degree of compaction of limestone.

This work aims to establish the importance of some of the above-mentioned parameters in the development of carbonate binders by cold sintering of limestone powder. Compressive strength measurements were used as an indicator of the efficiency of the cold sintering process.

Materials and methods

The limestone powder used in this work had the fineness of 53% passing through a 45 μm sieve. Industrial grade CO_2 was used throughout the work.

The equipment used to prepare samples is shown in Fig. 1. It consists of four cells (pellet dies) with internal diameters of 16 mm, and a hand-operated hydraulic press. CO_2 gas at the required pressure can be delivered to the die from a gas cylinder. Samples can be subjected to compaction and CO_2 pressures, as required, using this equipment.

The parameters and their ranges investigated in this study are as follows:

- CO_2 gas pressure—atmospheric, 10 and 35 atm
- CO_2 exposure time—0–90 min
- Post-compaction pressure—10 and 15 MPa
- Pressing time (post-compaction)—10, 30 and 60 min

The water/solid ratio by mass of the initial limestone compacts was kept constant at 0.2. (*This was found to be the least amount of water required to get the required consistency of the limestone/water mixture, while at the same time avoiding any leakage during the sample compaction under pressure*.) All experiments were carried out at laboratory temperature (23 ± 1 °C).

To make the limestone compacts, a known amount of limestone/water mixture was placed into the cells and compacted loosely by applying a low pressure (2 MPa) for 30 s. This was to obtain the consistency in pore structure/porosity of the compacts before exposure to CO_2. (It was

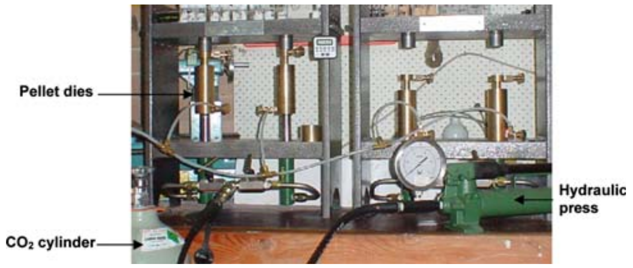

Fig. 1 Equipment used to prepare limestone compacts

assumed that at this level of compaction, CO_2 would be distributed throughout the compacts, allowing 100% exposure of particles to the gas). The compaction pressure was released and the compacts were exposed to chosen CO_2 pressures for various periods of time. They were then pressed (post-compaction) under high compaction pressure for various time periods. The compacts were taken out and kept at 23 ± 2 °C and 50 ± 5% RH for 7 days before testing for compressive strength. (The amount of sample was chosen so that the final compacts had a similar height of ~25 mm. This produced cylindrical samples of a height/diameter ratio of around 1.5.) For each compressive strength measurement, the average value of two or three compacts was considered.

Fractured samples of the resulting products were also examined using SEM for microstructural developments.

Control samples were prepared, which were directly subjected to the relevant post-compaction pressures for different time periods, without applying 2 MPa pressure for 30 s at the beginning, as for the samples exposed to CO_2 gas pressure. It was assumed that the elimination of this step would have no impact on the final strength of the control samples.

Results

Compressive strength

The compressive strengths of the different mix formulations and the respective control samples are given in Table 1. For the different mix formulations, the percentage strength increase, with respect to the control sample, is also shown. The compressive strength development of studied mix formulations are also shown in Figs. 2–5.

Samples exposed to 10 atm CO_2 pressure did not show any significant change in strength, but those exposed to 35 atm CO_2 pressure for the same period of time (30 min), showed about a 30% strength increase compared to the control (Set 1—Fig. 2). Samples exposed to 35 atm CO_2 pressure for 30 min and subsequently compacted at 10 or 15 MPa showed that increasing the compaction pressure improved strength characteristics (Sets 2 & 4—Fig. 3). Longer pressing times also favoured the strength characteristics of the limestone compacts. This was observed irrespective of the compaction pressure applied (Sets 3 & 5—Fig. 4). However, increasing CO_2 exposure times did not have any additional benefit on strength development (Set 5—Fig. 5). The strength improvement was 14%, 17% and 15% for exposure times of 30, 60 and 90 min, respectively.

The results also demonstrate that post-compaction pressure alone had a small impact on strength gain, as shown by the control samples (Sets 2, 4 and 5). However, when the limestone powder was subjected to CO_2 pressure and subsequently pressed at high compaction pressure, further improvements of strength compared to the controls were clearly visible. This indicates that a binding process between particles takes place during the final compaction as a result of the CO_2 exposure. The results also show that the extent of strength improvement depends on the experimental conditions. The strength increases with:

Table 1 Compressive strengths of different mix formulations

Set no.	CO_2 treatment		Post-compaction		Compressive strength (MPa)		Per cent strength increase from control	Figure number
	Pressure (atm)	Exposure time (min)	Pressure (MPa)	Pressed time (min)	Control (only subjected to post-compaction)	CO_2 exposed sample		
1	10	30	15	30	9.5	9.3	0	Fig. 2
	35	30	15	30	9.5	12.4	30	
2	35	30	10	10	7.8	8.4	7	Fig. 3a
	35	30	15	10	8.9	10.2	14	
3	35	30	10	10	7.8	8.4	7	Fig. 4b
	35	30	10	30	7.5	9.0	19	
4	35	30	10	30	7.5	9.0	19	Fig. 3b
	35	30	15	30	9.5	12.4	30	
5	35	30	15	10	8.9	10.2	14	Fig. 4a
	35	30	15	30	9.5	12.4	30	
	35	30	15	60	9.5	11.7	23	
6	35	30	15	10	8.9	10.2	14	Fig. 5
	35	60	15	10	8.9	10.4	17	
	35	90	15	10	8.9	10.2	15	

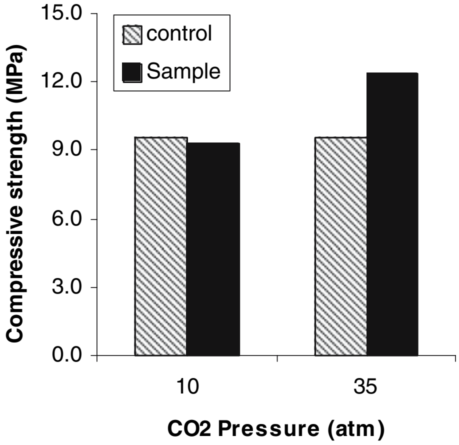

Fig. 2 Strength development at different CO_2 pressure

- Increasing CO_2 gas pressure.
- Increasing post-compaction pressure combined with longer pressing time.

Increasing exposure time beyond 30 min did not have any significant effect on strength improvement.

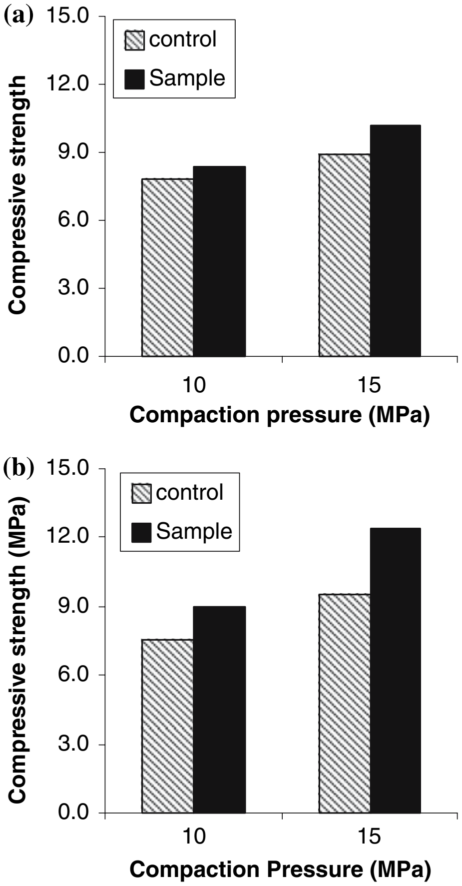

Fig. 3 Strength development at different post-compaction pressures (**a**) 10 min pressing time; (**b**) 30 min pressing time

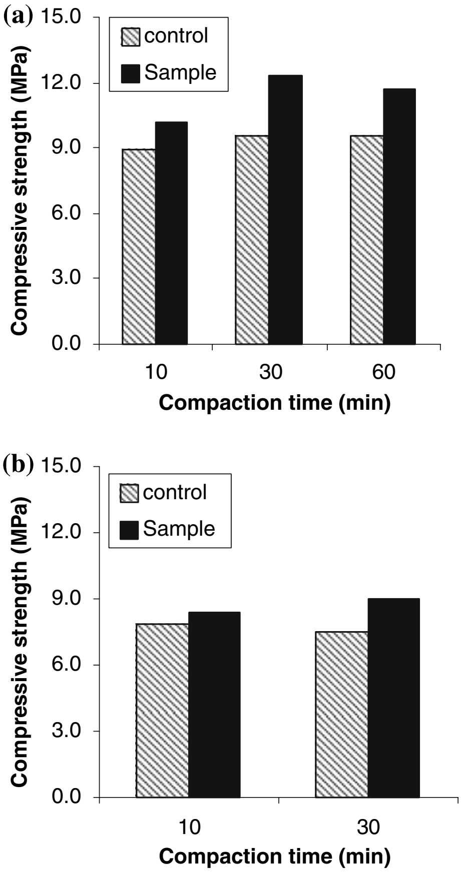

Fig. 4 Strength development at changing pressing times (**a**) compaction at 15 MPa; (**b**) compaction at 10 MPa

From the range of experimental parameters studied in this work, the maximum strength increase (30%) was obtained with the samples exposed to 35 atm CO_2 pressure for 30 min, followed by 30 min pressing time at 15 MPa compaction pressure.

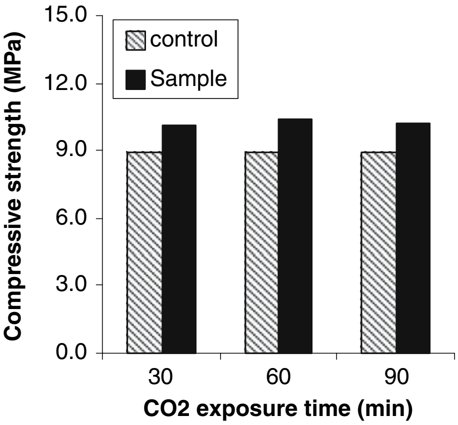

Fig. 5 Strength development at different CO_2 exposure times

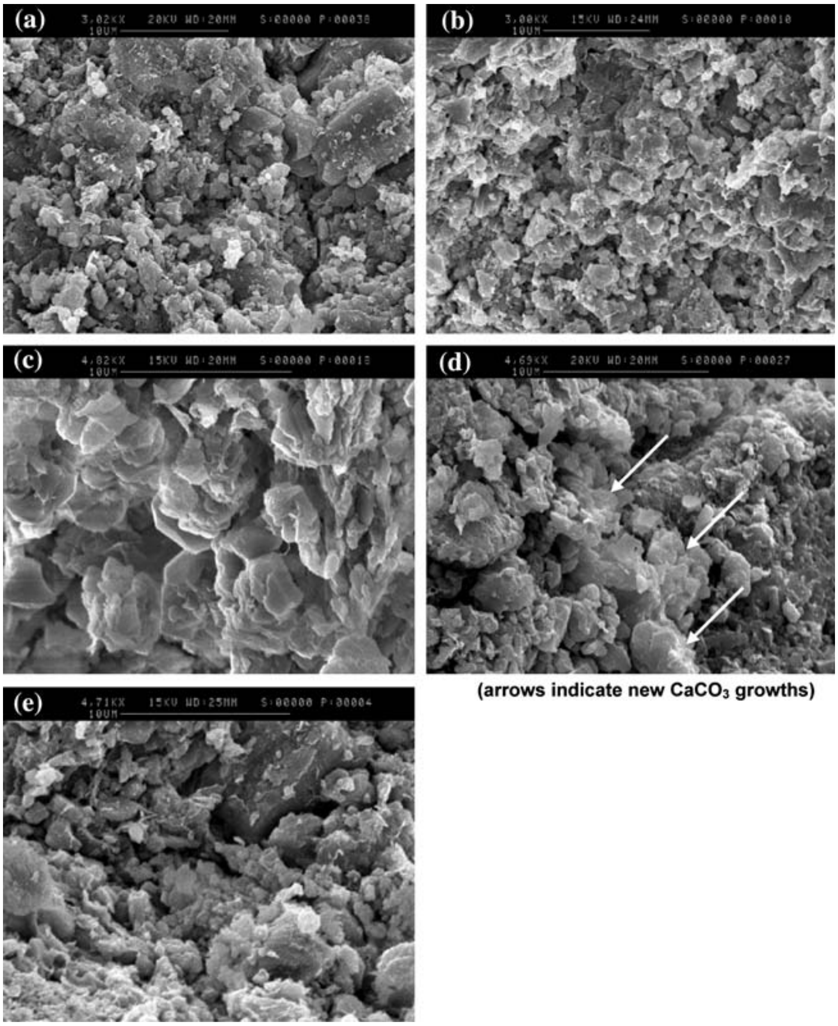

Fig. 6 SEM of the control sample (**a**), (**e**), and sample exposed to 35 atm CO_2 pressure followed by 15 MPa compaction pressure (**b**), (**c**), (**d**)

(arrows indicate new $CaCO_3$ growths)

Microstructure

The limestone compact that showed the maximum strength improvement (exposed to 35 atm CO_2 pressure for 30 min, followed by 15 MPa compaction pressure for 30 min) and its respective control sample (only subjected to 15 MPa compaction pressure for 30 min) were examined using scanning electron microscopy (SEM). Figure 6(a) and (b) present SEMs of the Control sample and the sample subjected to both CO_2 gas and compaction pressures respectively. The sample exposed to CO_2 is much denser, and $CaCO_3$ grains/particles appear to be more interconnected, giving a less porous structure. Figure 6(c) presents a higher magnification of this less porous structure. This network-like structure is not a clear feature in the control sample, and separate $CaCO_3$ grains of different sizes (including larger grains of about 10 µm in size) can be identified. These observations were found with all the specimens examined.

Another feature observed in the microstructure of the samples exposed to both CO_2 and compaction pressure is the presence of bundles of calcium carbonate crystal growths with defined shape (Fig. 6(d)), which were absent or not dominant in the control sample (Fig. 6(e)). These are possibly newly formed $CaCO_3$ growths as a result of the dissolution and re-precipitation mechanism. This data, therefore, indicates that exposure to CO_2 gas pressure followed by post-compaction changes the microstructure of limestone compacts.

Discussion

The results presented demonstrate that carbonate binder formation by cold sintering of limestone powder is possible. The efficiency of the process depends on various experimental parameters.

As expected, higher CO_2 pressures facilitate the dissolution of $CaCO_3$, and the best strength improvements were obtained at the maximum CO_2 gas pressure (35 atm) investigated in this work. Increasing CO_2 exposure time beyond 30 min did not have any added advantage, perhaps indicating that maximum dissolution was achieved within 30 min of exposure. It should be noted that in the methodology used, the amount of water available for the dissolution was fixed, which therefore limits the amount of calcium carbonate available for reprecipitation (or recrystallisation) and possibly the quantity of the cementing phase. (At increased water contents, more $CaCO_3$ has to be dissolved to reach the equilibrium and this in turn makes more $CaCO_3$ available for reprecipitation.)

Once $CaCO_3$ is dissolved in water, the application of post-compaction pressure is important, as it brings the particles close together and reprecipitation takes place on or in between grain contact points. It has been shown previously [8] that the efficiency (strength) of calcium carbonate binders depends mainly on the morphology and crystalline nature of the carbonate phase formed, and is related to the extent of compaction of the material. The present work also shows that the application of higher compaction pressures, preferably for a longer time, facilitates crystallisation and hence new binder formation.

It is also evident from the microstructural data that the application of CO_2 pressure is able to dissolve calcium carbonate grains (fully or only the surface), and large separate grains were mostly absent in these samples. The presence of newly formed calcium carbonate crystal growths in these samples are the result of a dissolution–reprecipitation process. The strength improvements obtained in these samples can be attributed to these crystal growths, which produce a network-like structure.

Overall, this work shows that cold sintering of limestone powder can result in new carbonate binders. The process is dependent on various parameters. One important requirement for the production of efficient carbonate binders from this process is the achievement of higher solubility of the limestone powder. The more $CaCO_3$ dissolved, the more is available for reprecipitation. Increasing the CO_2 pressure beyond 35 atm is perhaps one way of achieving this. The particle size of the limestone powder is another important factor to be considered, as it can have an impact on both solubility and the pore structure of the compact, and hence the accessibility to CO_2 gas. The amount of water that can be used in a compact is limited in this methodology, and therefore controls the amount of $CaCO_3$ available for the cementing process.

Conclusions

Carbonate binders can be obtained from cold sintering of limestone powder under controlled experimental conditions. High CO_2 pressures combined with high post-compaction pressures facilitate the formation of a new calcium carbonate phase that binds the powder particles to an agglomerate. The amount of dissolved limestone available for the reprecipitation is an important factor determining the efficiency of the process and the strength of the binder.

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