

Review

A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂

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Abstract

Moist calcium silicate minerals are known to readily react with carbon dioxide (CO₂). The reaction products can cause rapid hardening and result in the production of monolithic materials. Today, accelerated carbonation is a developing technology, which may have potential for the treatment of wastes and contaminated soils and for the sequestration of CO₂, an important greenhouse gas. This paper reviews recent developments in this emerging technology and provides information on the parameters that control the process. The effects of the accelerated carbonation reaction on the solid phase are discussed and future potential applications of this technology are also considered.

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1. Introduction

Carbonation is a natural phenomenon affecting commonly used cementitious materials, which can have detrimental effects on structural concrete. On the other hand, carbonation has been demonstrated to act positively in the immobilisation of heavy metal-contaminated soils and other residues [1–5]. In this patented application [6,7], the use of carbonation has been used to overcome the inhibiting effects of complex waste materials on the hydraulic and pozzolanic reactions responsible for effective solidification [6].

The *accelerated carbonation* of hazardous wastes is a controlled accelerated version of the naturally occurring process. The solid mixture is carbonated under a gaseous, carbon dioxide (CO₂)-rich environment, which promotes rapid stiffening of the green product into a structural medium within minutes [8]. In addition, in many cases, binding of toxic metals may occur as the carbonated product rapidly solidifies. The consequent significant improvement in the chemical and physical properties of certain treated materials can facilitate re-use in a variety of construction applications.

At a time when rapidly changing legislation is promoting the recycling and re-use of waste materials, the emergence of technologies that can utilise both gaseous and solid waste products in re-useable materials is timely. Thus, this paper reviews the current state of the art and potential future developments in the application of accelerated carbonation technology.

2. Applications of carbonation

2.1. Natural carbonation

The utilisation of natural carbonation for the formation of carbonated cementitious systems is not new. Man has used alkaline earth hydroxide cements and mortars, which harden due to their reaction with atmospheric CO₂, for thousand of years. However, the development of strength in these calcareous cements is slow and uneven due to the low partial pressure of CO₂ in the atmosphere (which is only 0.03–0.06% v/v), and the slow rate of diffusion of CO₂ into mortar [9].

In service, ordinary Portland cement (OPC)-based materials are usually exposed to percolating ground water or infiltrated rainwater and are therefore subject to corrosion. If

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the water contains CO_2 , the effect is that carbonic acid neutralises the alkalis in the pore water. The calcium silicate hydrate gel (C–S–H), which is the dominant hydration product resulting from normal hydration of PC, is dissolved by the acidic environment, consequently affecting the leachability characteristics and the durability of cementitious products over time. As acid attack proceeds, a considerable amount of dissolution of primary cementitious phases and the precipitation of secondary phases results. The main secondary mineral, CaCO_3 , is formed by the combination of moist CO_2 with Ca^{2+} , is mobilised via the dissolution of calcium hydroxide (portlandite), and from the decalcification of the gel phase, C–S–H¹ [10] to leave silicate hydrate.

2.2. Effect of carbonation on the durability of hardened cement-based products

Reinforcement corrosion is the most important durability problem of structural concrete. In general, the cement present in the concrete hydrates giving a highly alkaline medium (ca. pH 13). This confers a chemical protection to steel through a passive protective oxide film, formed in an environment at or above a pH of 10.5. Carbonation of concrete can destroy this passive oxide film leaving the steel exposed to corrosion [11].

2.3. Accelerated curing of compacted cementitious systems by carbonation

When applied to compacted systems, such as mortars, carbonation takes place mainly in the outer portions of monoliths. The initial reaction on exposure to CO_2 appears to be an accelerated hydration of the silicates to form a C–S–H-like gel and calcite. After 3 min of carbonation, the amount of C_3S reacted is similar to that after 12 h of hydration [12].

The stoichiometry of the initially formed C–S–H gel is similar to that found in conventional hydration. Further reaction results in progressive carbonation of the gel with the consequent decrease in its content of calcium. However, the strength development in the compacted mortar exposed to CO_2 is much more rapid than during normal hydration [12], and experiments have shown that approximately 1000 kg/cm^2 is obtained within 15 min in carbonated Portland cement paste, confirming the potential of carbonation to accelerating the hardening of thin-walled materials [13].

2.4. Carbonation as a stabilisation/solidification technique

Cement-based solidification using hydraulic or pozzolanic binders is used for the immobilisation of soils and sludges containing a variety of metal pollutants. Solidification with cementitious materials is attractive because it offers an

assurance of chemical stabilisation (at high pH) of many compounds and produces a mechanically stable waste form. It is a recognised way of disposing of solid wastes [14] and even water contaminated with toxic heavy metals [1].

Solidification can be defined as the chemical binding process, which binds toxic waste matter into solid bulks or physically cuts them off from the outside by forming a capsule. It is a process that converts potentially toxic waste materials into less toxic solid materials before landfilling [15]. The choice of binder is a balance between cost and environmental considerations. The more C_3S or calcium the binder contains, the higher the potential for producing a carbonated product.

In the UK, over three-quarters of the waste produced in the Thames Region, including London (the biggest producer of waste), ends up in landfill sites. This amounts to 22 million tonnes per year and comprises household, industrial and commercial waste streams. It is estimated that the landfill sites for the South East of England will be at full capacity by 2005 and problems with leaching will occur. Furthermore, legislation restricting disposal to landfill is driving the growing interest in stabilisation/solidification for re-cycling certain waste materials, including the products of incineration or composting [16].

2.4.1. Stabilisation of wastes by carbonation

Cement-solidified hazardous wastes are susceptible to carbonation. Carbonating the solidified waste before landfill lowers the pH to values corresponding with the minimum solubility of many heavy metals and to within regulatory defined limits (pH < 9.5). This leads to general improvements in metal immobilisation. However, the reduction of the buffering capacity of the solidified matrix due to the lowered alkalinity makes the waste more vulnerable to the effects of acid attack and, hence, to the release of heavy metals in the long term [17], especially where open containment systems are employed. Carbonation also increases the acid neutralising capacity (ANC) of the material under acidic conditions. For instance, the ANC of bottom ash was increased from 0.46–0.48 meq/g to 0.88 meq/g (at pH 5) after 48 h accelerated carbonation [18]. Carbonation of cement–waste mixtures leads to changes in the microstructure, increase the strength values (based on non-confined crushing tests) by up to 70% higher and can decrease the leaching of metals. Materials that have been utilised in either laboratory or pilot-scale evaluations using accelerated carbonation technology are given in Table 1.

The carbonation of solidified low-level radioactive wastes has also been studied. It has been found that some radionuclides pass through the carbonated zone and may react forming a solid solution with calcite [19].

2.4.2. Stabilisation of contaminated soils by carbonation

The contamination associated with derelict land can also be treated using waste CO_2 . By using CO_2 gas at

¹ Nomenclature used in this work: C=CaO, S=SiO₂, H=H₂O, $\bar{\text{S}}$ =SO₄, A=Al₂O₃, $\bar{\text{C}}$ =CO₂

Table 1
Wastes that have been utilised by carbonation and their usual disposal routes

| Waste | Description | Usual disposal routes |
|--------------------------------|---|---|
| Slag | Secondary products from metal refining. | Aggregate manufacturing. |
| BFS | Granulated blast furnace slag. | Cement production and concrete admixture. |
| SS | Steel production. | Amour stone and soil conditioning. |
| Galligu | By-product of the manufacture of sodium carbonate. | Dumped to pits and covered with ash. |
| MSWI ash | Ash from combustion of municipal solid wastes. There are two kinds, bottom and fly ashes. | Disposed of in landfills. Incorporation into materials for construction applications. |
| Deinking ash | Ash from paper recycling process. | Dumped to landfill. |
| Cyclone dust | Air pollution control waste. | Landfilled. |
| Cupola furnace dust | Waste dust coming from furnace for metal casting. | Landfilled. |
| Filter cake | Residue deposited on a permeable medium when slurry is forced against the medium under pressure. | Landfilled in general. Certain treatments depend on the nature of the cake. |
| Pulverised fly ash | Powder of burnt coal in thermal power stations. | Additive in the building industry. |
| Cupola arrester filter cake | The insoluble residue deposited on the air pollution control devices of a cupola furnace. | Landfilled. |
| Sewage sludge ash | By-product produced during the combustion of dewatered sewage sludge in an incinerator. | Landfilled, concrete production, mineral filler and soil conditioner. |
| Sewage sludge | Waste product from wastewater treatment. | Stabilisation with cement. |
| Cement kiln dust | Partially calcined mineral mixture. | Landfilled. Agricultural applications. |
| Air pollution control residues | Combined material collected either in electrostatic precipitators or fabric filter devices. | Landfilled and used for cement production. |
| Coal fly ash | Residue coming from coal burning power plants. | Cement products and landfilled. |
| Arc furnace dust | Largest solid waste stream produced by steel mills. | Recycled and landfilled. |
| Thermal reclaim dust | Dust coming from the breaking of the sand treated in the reclaim units for its re-use in casting processes. | Used as fillers, for concrete manufacturing, for asphalt manufacturing. |
| Fettling shop extraction dust | Dust coming from the lining of castings in a puddling furnace. | Recycled in-plant and landfilled. |
| Shot-blast dust | By-product from the cleaning of finished castings. | Used as roadbase and the rest landfilled. |
| Bag-house dust | Bag-house dusts are collected from emissions from the furnace or sand reclamation plant. | Landfilled. Used as raw material for cement and concrete manufacturing. |
| Foundry sands | By-product of the foundry casting process of metals. | Partly re-used and partly landfilled. |
| Blast furnace flue dust | Filter sludge from wet cleaning plants from foundry, iron and steel industries. | Part recycled, and the rest sent to landfill. |
| Melting dust | By-product of the molten metal injection processes. | Mostly recycled. |
| Mill scale | Filter dust from sand regeneration and fettling shop plants. | Landfilled and recycled. |
| Silica pot liner | Waste product of the electrolytic process in the smelting of aluminium. | Vitrified and landfilled. |
| Coke breeze | Filter dust from hall dust extraction plants. | Mostly recycled and the rest landfilled or land applied. |

atmospheric or slightly positive pressure, and carbonating with it a mixture of the contaminated soil and an appropriate binder, the reaction can be carried out within a few minutes. Suitable binders are Portland cement, quick lime, slaked lime and a variety of waste products, including slag. In addition, there are naturally occurring calcium silicate minerals that also have potential for carbonation [20].

The major advantage of this treatment over conventional solidification/stabilisation systems, in which long curing time may be required, is that with carbonation the soil is immediately available for development. The carbonation technique underwent successful pilot-scale field trials in September 2000 when accelerated carbonation was applied at an ex-pyrotechnics site at Dartford in Kent [21]. Soil on the site had general elevated levels of heavy metals, with isolated contaminant hotspots across the site [22].

2.5. Recycling of waste streams

Accelerated carbonation reactions can also be suitable for the treatment of non-hazardous waste streams to improve their re-use in some way. For instance, powdered materials with appropriate chemical properties and high surface areas for reaction could be solidified to produce useful products.

A known application is the recycling of concrete waste produced by demolition of concrete structures. Through carbonation, the waste is consolidated and a solid material with greater strength is produced [23].

Fig. 1 shows SEM images of concrete samples before and after carbonation. The image of the treated sample (Fig. 1b) shows the granular-textured calcite that has precipitated between the platy particles of the initial mineral, and a higher density can be appreciated. Regarding the recycling of

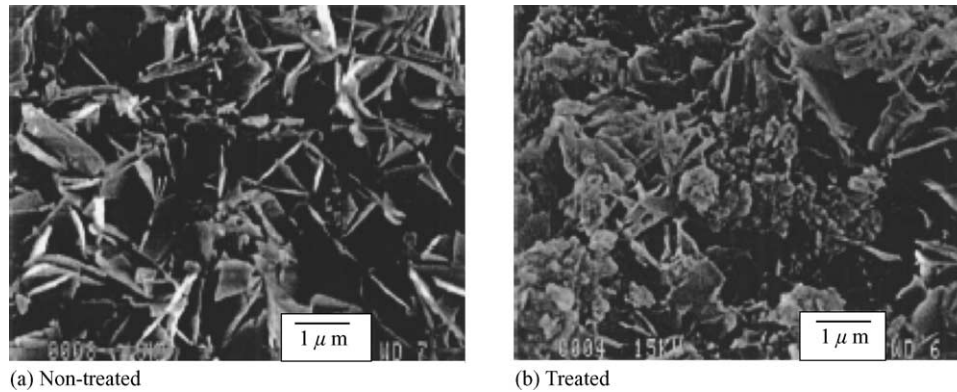


Fig. 1. SEM micrographs of autoclaved light weight concrete samples (a) before and (b) after CO_2 solidification reaction [23].

hazardous and non-hazardous wastes, if treatment by accelerated carbonation is considered, a number of factors have to be evaluated, including the durability of the treated product and the re-use options defined under current law.

3. The carbonation: process requirements and reactions

For a solid to be suitable for accelerated carbonation, it must have certain chemical and physical properties that make it suitable for treatment.

3.1. Definition of the carbonation reaction

Ionised carbon dioxide induces solvation of calcium ions from the solid phases, which then re-precipitate in the pore space of the mixture as CaCO_3 , forming a solidified product [8]. This process is strongly exothermic.

The reaction is diffusion-controlled. The gas diffuses into the solid resulting in a growing front of carbonated material surrounding an inner zone of non-carbonated material. The conceptual model for the reaction of carbon dioxide with a waste form is presented in Fig. 2.

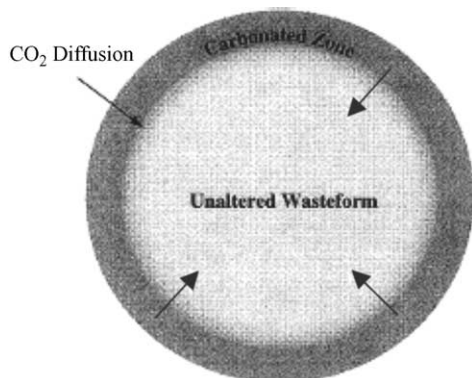


Fig. 2. Schematic of carbonation process [5].

3.2. Reaction mechanism

The following is the sequential mechanism that takes place during the carbonation of cementitious materials. Fig. 3 illustrates this mechanism, showing all the individual steps.

The individual steps in the sequence are [24]:

1. Diffusion of CO_2 in air.
2. Permeation of CO_2 through the solid.
3. Solvation of $\text{CO}_{2(\text{g})}$ to $\text{CO}_{2(\text{aq})}$. Boundary layer transfer is favoured by a high internal surface area of solid.
4. Hydration of $\text{CO}_{2(\text{aq})}$ to H_2CO_3 . This is a slow, rate-determining step.
5. Ionisation of H_2CO_3 to H^+ , HCO_3^- , CO_3^{2-} . This occurs almost instantaneously, making the pH fall by approximately 3 units, typically from 11 to 8.
6. Dissolution of cementitious phases C_3S and C_2S . Because the process is cyclic, this step is rapid and extensive, and generates a considerable exotherm. The calcium silicate grains are covered by a loose layer of calcium silicate hydrate gel, which is quickly dissolved, releasing Ca^{2+} and SiO_4^{4-} ions.

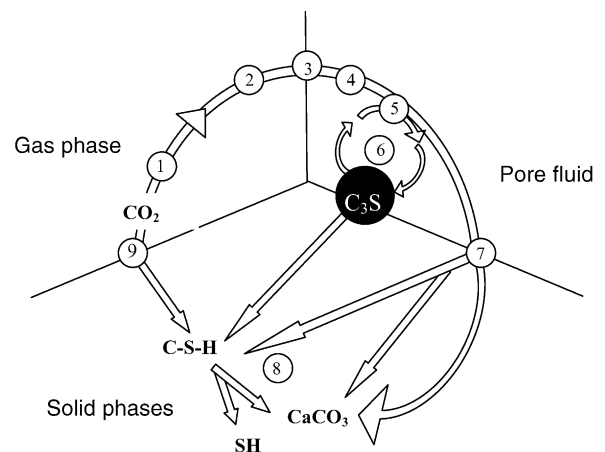
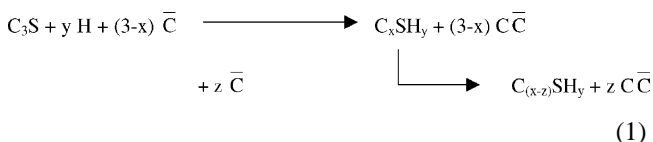


Fig. 3. Proposed mechanism for accelerated carbonation. Adapted from [24].

7. Nucleation of CaCO₃, C–S–H. The nucleation is favoured by slightly high temperatures and the presence of finely divided material, which acts like heterogeneous nuclei.
8. Precipitation of solid phases. At the beginning, vaterite and aragonite can be formed, but these polymorphs of CaCO₃ ultimately revert to calcite. Amorphous calcium carbonate can be found in the final product.
9. Secondary carbonation. C–S–H gel forms and is progressively decalcified, converting ultimately to S–H and CaCO₃.

3.3. Reactions

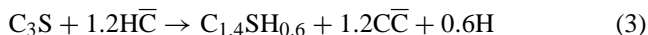
The overall stoichiometry of the carbonation reaction of the major OPC silicate phases in cement indicates that initial carbonation is accompanied by hydration and is followed, after some delay, by secondary carbonation [14]



The mechanism of reaction proposed above is based on the knowledge of the behaviour of C₃S during normal hydration. C₂S reacts similarly. First, carbon dioxide dissolves in water to form carbonic acid. This reaction involves the evolution of considerable quantities of heat 669.9×10^3 J/mol [9]

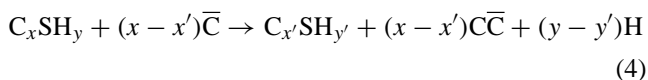


The carbonic acid promotes a vigorous reaction of C₃S in the first 3 min [12]



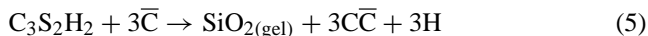
C₂S reacts similarly. The formation of crystalline CaCO₃ is also an exothermic reaction which releases 1205.8×10^3 J/mol [9].

After 3 min, carbonation of the gel is the major reaction, implying a change in composition [12].



After that, further carbonation occurs changing the composition of the gel.

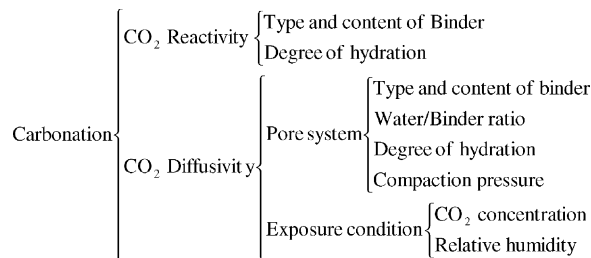
The C–S–H is completely decalcified and finally transformed into calcium carbonate and highly polymerised silica gel. This gel is acid stable and maintains a similar morphology to the original hydrate [25]



3.4. Variables influencing the carbonation process

The extent and quality of carbonation, as well as the fixation and immobilisation of specific contaminants, depend

upon several parameters. The main ones are the diffusivity and reactivity of CO₂. The following is a scheme of what these factors depend on:



3.4.1. Reactivity of CO₂

For CO₂ to be reactive in order to achieve an effective carbonation, the solid must have certain chemical properties, which are shown in Table 2.

The following is an explanation of how the amount and composition of the reactants (solid, water and carbon dioxide) affect the reactivity of the system.

Solid composition: The existence of certain cementitious phases and specific metals in the waste might influence the rate of the carbonation reaction and therefore, the amount of calcium carbonate formed [14]. Some metals, such as Pb, Cd, Ni, can cause an increase in permeability and pore size distribution, causing a decrease of the alkaline buffering capacity of the cementitious solid, a degree of decalcification of the anhydrous calcium silicate phases and an acceleration of hydration. Experimental studies have shown that the amount of calcium carbonate deposited in carbonated metal-doped solid can be up to 40% higher than in samples that have not been doped [10].

There are also elements that influence the carbonation negatively, such as organics and anions, which can react and affect the effective diffusion coefficient of CO₂. The composition of the solid phase can give an idea of the extent of carbonation that can be achieved [29].

Water content: Water is necessary to promote the reaction of CO₂, but too much water limits the reaction due to the blockage of the pores in the solid. The water takes part in the solvation and hydration of the carbon dioxide. It dissolves the Ca²⁺ ions from the solid that will react to form the CaCO₃. Therefore, it influences the amount of product generated, which is also related to the strength development.

Electrochemical investigations and studies by X-ray methods have shown that at high water-to-cement ratios (w/c), ranging between 2 and 4, the acidity and resistance of the solution increase sharply after admission of carbon dioxide, which is evidence of effective penetration of CO₂ into such pastes (see Fig. 4). However, strong materials can not be obtained at high w/c ratios. At w/c ratios from 0.28 to 0.4, CO₂ does not diffuse into the depth of the material. At low w/c ratios, the gas permeability is increased and the CO₂ effectively diffuses into the material. Hence, the optimum ratio has been found to be between w/s 0.06 and 0.20 [13,30,31].

Table 2
Chemical properties required for effective carbonation

| Property | Requirement |
|---------------------------------------|---|
| Solid composition | Materials must be inorganic in nature, containing calcium and/or silicon salts. They may be hydraulic, pozzolanic, lime-bearing or other CO ₂ -reactive calcium-containing material heavy metals. |
| pH | The alkaline environment of the solid causes metals hydroxides to form carbonates in the presence of CO ₂ . |
| Ca content | Carbonation is known to occur in materials which have available Ca. The higher the concentration of Ca in the material, the better the result of carbonation [26]. |
| Ca/Si ratio | The higher the ratio, the higher the degree of carbonation [27]. |
| Ferrite/C ₃ A | The presence of these phases is important to the formation of ettringite, which in the presence of CO ₂ decomposes to form gypsum, calcium carbonate and alumina gel [14]. |
| Organics and anions | The carbonation is affected by their presence in the solid [14]. |
| Certain heavy metals (Pb, Cd, and Ni) | Increase the susceptibility of cementitious materials to carbonation. |
| Free water content | Some water is necessary for the reaction, but an excess of water limits the rate of carbonation. Materials with high initial free water contents have increased gas permeability, letting more CO ₂ enter the solid. However, as the pores are filled with water, the penetration of CO ₂ is hindered as the rate of diffusion of CO ₂ is reduced. In addition, there is a lower strength development. |
| Microstructure | Higher microporosity of the hydration products, leads to a better carbonated material. |
| Specific surface area | Materials with lower surface need less water to have optimum carbonation [28]. |
| Permeability | When the gas-permeability of the cementitious material is high, CO ₂ penetration is enhanced facilitating carbonation. |

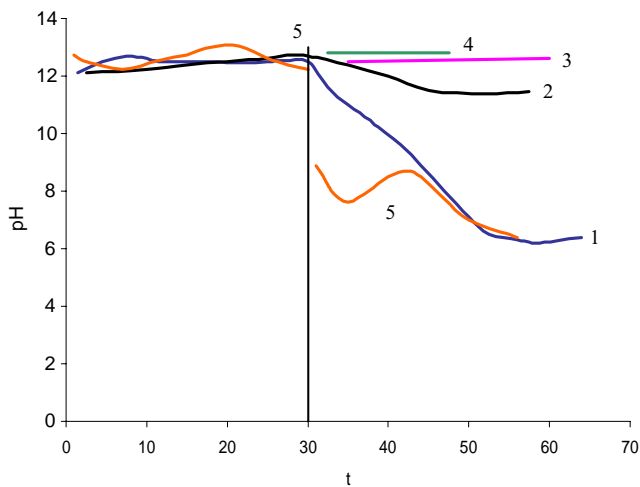


Fig. 4. Curves for the course of variation of hydrogen-ion concentration (pH) in a CO₂ atmosphere at various water–cement ratios (w/c ratio): (1) 4.0; (2) 2.0; (3) 0.4; (4) 0.28; (5) 0.12. Adapted from [13].

Over w/s 0.25, the reaction is effectively slowed down and the CO₂ uptake is low although Yousuf et al. reported to have successfully carbonated with values up to 0.35 [25]. Lange et al. also showed that different water contents (in some cases higher than 0.2) are required for different cement types in order to achieve the same degree of carbonation [14].

3.4.2. CO₂ diffusivity

Diffusivity of CO₂ is constrained by physical properties of the solid. Table 3 shows the major physical properties affecting carbonation.

Compaction pressure: The forming compaction pressure of the granular/powdered material prior to carbonation also influences the resultant product. The porosity and permeability of the solid decrease when the compaction pressure is increased, which leads to greater strength development. Conversely, the low porosity inhibits the diffusion of the CO₂ into the solid. Thus, the amount of precipitated CaCO₃ is lower, resulting in lower strength development.

Fig. 5 shows the dependence of the strength of carbonated specimens on the compaction pressure. It can be seen that,

Table 3
Physical characteristics of the solid that influence carbonation

| Feature | Effect on carbonation |
|---------------------------------|--|
| Size | Finer powders generally show greater degree of carbonation at higher water contents, since there are more surfaces to react with CO ₂ . Nevertheless, when there are differences in the degree of carbonation between the distinct size fractions of the same material, it is generally due to their different compositions. Smaller size fractions carbonate better because they are higher in CaO [32]. |
| Surface area | The higher it is the greater is the extent of the carbonation reaction. |
| Porosity | Low porosity impedes CO ₂ diffusion between particles [26,33] and is often related to high degrees of compaction. |
| Permeability to CO ₂ | Affects the diffusion of CO ₂ inside the material and the solubility of phases. Materials with high free water content have lower strength and higher permeability. |

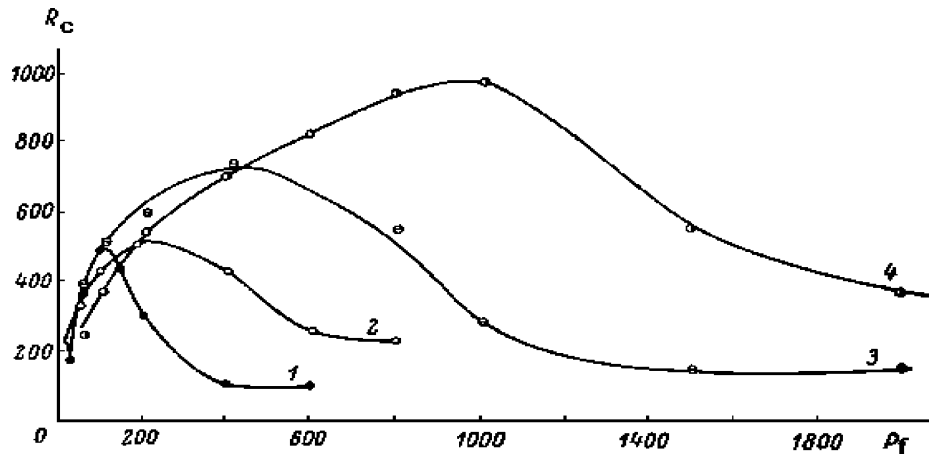


Fig. 5. Dependence of the strength R_C (kg/cm^2 ; $\cdot 9.81 \times 10^4 \text{ Pa}$) of carbonated specimens of various w/c ratios, on the forming compaction pressure P_f (kg/cm^2). w/c ratio: (1) 0.14; (2) 0.12; (3) 0.1; (4) 0.08. From [13].

Table 4
Effect of the exposure conditions on the carbonation process

| Conditions | Effect |
|----------------------------------|--|
| CO ₂ partial pressure | The higher the amount of CO ₂ in the gas phase, the higher is the rate of carbonation. However, excess CO ₂ pressure does not lead to a higher strength of carbonated product [13] (slower reaction would allow for dissipation of heat and reduce stresses on the product). Thus, by varying the partial pressure of CO ₂ , the rate of carbonation can be controlled and so can the compressive strength [9]. |
| Relative humidity | Carbonation is more rapid at a relative humidity of 50–70% and decreases at higher and lower relative humidities [4,34]. As explained before, the diffusion of CO ₂ and the reaction kinetics are two conflicting processes, so a compromise in the value of this factor has to be found. |
| Temperature | The uptake of CO ₂ increases with increasing temperature up to 60 °C (at atmospheric pressure) [23]. This is most likely due to the leaching of Ca ²⁺ ions from the particles of the solid. Higher temperatures decrease the solubility of CO ₂ in water, therefore decreasing the rate of carbonation. However, as the carbonation reaction is exothermic, the heat of reaction promotes the formation of meta-stable forms of CaCO ₃ . To obtain the desired stable polymorph (i.e. calcite) the process should be maintained at low temperatures – in the range 0–10 °C. Tests have shown that more calcite is formed if very cold carbonic acid is used for carbonation [30]. Therefore, an optimum for this factor is required. |
| Pressure | A slight positive pressure of CO ₂ increases the rate of reaction and influences the strength development. Carbonation has been carried out at low and high pressures, under vacuum conditions and by supercritical carbon dioxide (scCO ₂). |

for each water–cement ratio, the strength reaches a maximum, indicating that, for any w/c ratio, there is particular compressive force at which the cement grains can be accessed by the CO₂ [13].

Exposure conditions: The effect of the main features of the exposure conditions on the carbonation process are shown in Table 4.

4. The results of carbonation

The result of the carbonation reactions are summarised as follows:

- An acceleration of normal and retarded hydration
- The precipitation of calcite in pore space
- A decalcification of residual cement grains resulting in the selective uptake of certain metallic species
- The precipitation of calcium–metal double salts

- The increased polymerisation of silicate phases
- The formation of metal–silicate complexes

Therefore, the products arising from carbonation induce important physical and chemical changes on the waste material being treated. A detailed explanation of these consequences now follows.

4.1. CO₂ consumption

Pressed ground stainless steel slag has been found to react readily at low pressure with approximately 18% of its own weight of CO₂ [32]. Other experiments have shown that up to 50% w/w consumption of CO₂ can be realised following repeated carbonation steps [20]. Jones considers the amount of CO₂ consumed is equivalent to the quantity of calcium hydroxide that is present in the hydrated cement paste [35]; however, C–S–H and aluminates phases may also be carbonated. Nevertheless, carbonation seems to be an effective

Table 5
Variations in certain physical properties due to carbonation

| Characteristic | Consequence |
|------------------------|--|
| Permeability | It changes due to volume changes and density. |
| Contaminants | The effect of carbonation could be either beneficial or adverse on trace element mobility in cement-based systems. Contaminants may be absorbed into hydration reaction products, kept insoluble by the high pH environment of the system (typically pH < 10) and/or physically encapsulated in the cement matrices. Therefore, through carbonation metals that could be hazardous, such as Pb, Cd, Mo, Zn and Ni may be converted into their less soluble salts and immobilised [20]. |
| Hydration | It is accelerated. Cementitious compounds considered as poorly hydraulic for practical use are activated by the CO ₂ . Carbonation produces carbonate cementation and, as a result, an increase in compressive strength. Materials become less susceptible to shrinkage, and there is an improvement in structural integrity. |
| Strength | The strength developed in a cement solidified waste cured in a 100% CO ₂ atmosphere is 45% higher than that developed when cured in a nitrogen atmosphere. Values of compressive strength up to 7.9 MPa have been found in these systems [36]. |
| Porosity | It tends to drop, as previously large, open pores fill with calcium carbonate, which has a higher molar volume than the initial calcium hydroxide. Unexpectedly, this leads to higher diffusion of the CO ₂ [4], perhaps due to shrinkage during carbonation or to variation of the pore system distribution to a larger average pore size. |
| Tortuosity | It is higher than in a non-carbonated solid, so carbonation may lead to more rapid leaching of some species. |
| Pore size distribution | A carbonated material can have approximately twice as much volume attributed to small pores as a non-carbonated one. The precipitated calcium carbonate has very low solubility and will therefore block the pore system. However, due to the volume expansion involved in the reaction, there will be microcracks in the carbonated zone [28]. |

method for the treatment of slag and the sequestration of CO₂.

Theoretical maximum CO₂ uptake capacity due to carbonation can be calculated as a function from the chemical composition of the original material using Steinoor formula [29] given in Eq. (6)

$$\text{CO}_2(\%) = 0.785(\text{CaO} - 0.7\text{SO}_3) + 1.09\text{Na}_2\text{O} + 0.93\text{K}_2\text{O} \quad (6)$$

4.2. Physical consequences

One of the main reactions, the carbonation of calcium hydroxide, is accompanied by an increase in solid volume [28], which is caused by the following reaction



Each mole of calcium hydroxide (specific gravity 2.24 g/mol, molar volume 33.0 ml) is converted to the

carbonate (specific gravity 2.71 g/ml, molar volume 36.9 ml) with a consequent 11.8% increase in solid volume. The calcium carbonate is precipitated in the pore structure of the matrix of the cementitious material and this increase in volume will lead to structural changes. Table 5 shows the consequences of carbonation in the solid material.

Fig. 6 shows how the pore volume of the carbonated sample is lower than the non-carbonated sample. Studies using image analysis on cement stabilised wastes have shown a decrease of up to 26% in the observable pore volume [28].

4.3. Microstructural changes

Portlandite is arranged in a crystalline structure, which is assumed to be intimately intergrown with the C–S–H [37]. The microstructure is characterised by the precipitation of calcite in the pores, the decalcified C–S–H gel, and the production of gypsum from the decomposition of ettringite.

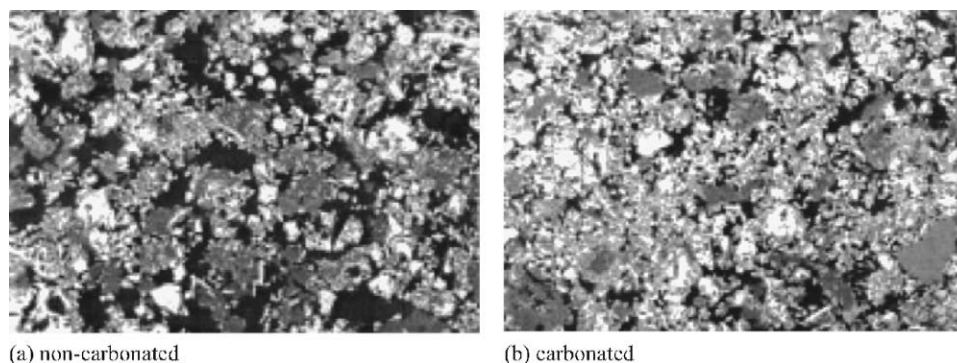


Fig. 6. General view of (a) non-carbonated and (b) carbonated samples [28].

During carbonation, the three polymorphs of calcium carbonate may be produced. The morphology of calcite is characterised by small, tightly packed crystals ($<3\ \mu\text{m}$) of acicular shape. Some microcracking is also noticeable [36] caused by the volume expansion during the reaction [28], while Lange et al. say that is the result of thermal stresses caused by heat generated during accelerated carbonation [36].

The C–S–H is not converted into silica gel by the reaction with CO_2 . This gel has an unbranched polymeric structure, and by means of carbonation, polymerization is promoted with a structural rearrangement [25] leading to a silica framework dominated structure.

After carbonation, a calcite-rich matrix filling the pores of the system can be observed when analysing wastes containing heavy metals. The residual non-carbonated grains are enveloped by a silica-rich decalcified rim which also encapsulates heavy metals such as Pb and Zn. Other metals such as Ni and Cr appeared to be immobilised in the calcite-filled porosity [36].

4.4. Chemical consequences

With progressive carbonation, the pH of the system gradually drops by around 3 units, leading to altered solubility (sometimes lower, sometimes higher) of contaminant metals solidified in the waste form [4]. The decrease in pH due to carbonation is dependent on the relation between the rate of dissolution of the solid calcium hydroxide through the following equation



and the rate of consumption of OH^- in the carbonation process [28]. When the solid $\text{Ca}(\text{OH})_2$ is consumed, the process becomes diffusion controlled, so the dissolution rate becomes slower. Consequently, a high concentration of hydroxide ions in the pore solution cannot be maintained when carbonation takes place [28]. There is also a change in the redox conditions. Carbonated systems are mildly reducing.

The ANC for carbonated systems increases under acidic conditions. Experimental work on carbonated municipal solid waste bottom ash has demonstrated that at pH 5, the ANC can double, reaching a value of 0.88 meq/g after 48 h of accelerated carbonation [18].

Heavy metal immobilisation in these systems can be related to either physical containment or chemical fixation. The lower solubility of some heavy metals in the alkaline pore solution explains the chemical fixation of heavy metals.

Alternatively, the major anions (i.e. nitrate, sulphate, chloride, fluoride) are usually incorporated in the lattice or in the interlayer regions of the hydration products including C–S–H. These products have low solubility at high pH conditions, but are unstable at the pH produced by the carbonation reaction ($\text{pH} = 7\text{--}8.5$) and dissolve, releasing their entrained anions. These anions will finally precipitate as salts which are readily leached by water [2].

4.5. Leaching behaviour

Due to changes in the microstructure, pH and redox conditions, there is a selective release of specific waste components (as in non-carbonated products). The effect of carbonation is twofold: some heavy metals form either hydroxi-carbonate or carbonate and deposit on the calcium silicates. Furthermore, for many metals the decrease in the pH reduces metal mobility, whilst for others there is an inversely proportional relationship between the pH and the leaching rate. For certain species, there is a stabilisation of metal carbonate precipitates, due to the provision of inorganic CO_2 , whilst at the same time there is an increase in the leaching rate due to the lowering of the pH.

Table 6 gives a summary of the behaviour of various species that can be present in the leachate of a carbonated solidified waste form. The leaching behaviour in hydrated and non-hydrated mixtures is differentiated, as they can perform in a different way.

5. Process methods

Different methods of carbonation including increased pressure, both in the presence and absence of steam, vacuum de-airing, use of low water contents and compaction of samples prior to carbonation. Hitherto technical limitations and high costs have prevented commercial development, but now the drivers have changed. The main factor that has led to the search for alternatives routes to carbonate cementitious materials is the dependence of the reaction on the content of water in the system so that there is enough water for the reaction without blocking the pores of the solid. Table 7 shows some of the methods of carbonation.

When carbonation is carried out under pressure in a static system, the penetration of CO_2 into the sample controls the reaction rate due to the lower vaporization of the water in the sample. At elevated pressures, larger amounts of gas are introduced throughout the sample before pore closure occurs, so carbonation is enhanced [9]. If the carbonation is attempted with dry CO_2 , water starvation results.

In a dynamic system, the reactivity of cementitious materials is enhanced, leading to a higher amount of carbonation achieved even at low pressures, whilst in static systems, at low pressures, the water vapour is trapped and saturates the CO_2 atmosphere. On the other hand, if the reaction is completed at near-vacuum conditions with the help of a desiccant, the water generated by the reaction maintains an open pore network. Nevertheless, only carbonation at near atmospheric pressures (1–5 bars) is considered here for practical, cost-effective applications.

5.1. Process scale-up

Accelerated carbonation is a technique with great potential to be industrialised. Pilot-scale trials have already been

Table 6
Behaviour of different species due to carbonation

| Species | Behaviour |
|-------------|---|
| Cu | In hydrated systems, carbonation in most cases increases Cu leachability due to (a) an increase in the solubility of the metal compounds through the reduction of the pH, (b) the decomposition of ettringite ($C_6AS_3H_{32}$) and (c) the polymerisation of the C–S–H releasing metal cations that were linked to the Si–O groups [1]. In other cases, lower leachability has been reported [38]. In non-hydrated systems, Cu is well retained [36]. However, in some cases, a higher leaching after carbonation has been observed, identifying $Cu_2(OH)_2CO_3$ as a possible solubility-controlling solid [39]. |
| Zn, Pb | In hydrated systems, they are moderately mobilised due to the lowering of the pH, although their concentration in the leachates is below the regulation limits [5,10]. These metals form either hydroxi-carbonates or carbonates that deposit on the calcium silicate minerals [1,10]. In comparison with other metals, they are the best retained species. Decreased leaching has even been reported for Pb due to the diminished amphoteric behaviour caused by the formation of sparingly soluble $PbCO_3$ [38,40]. In non-hydrated systems, the leaching of Pb is markedly decreased by carbonation as it is involved in sorption phenomena onto neoformed minerals [22,40]. On the other hand, Zn has shown positive results in some cases [22], while in others, the leaching is increased due to the dissolution of carbonate minerals at acidic pHs [39]. |
| Mn | The leaching of this metal is increased by carbonation [1]. |
| Ni, Cd, Co | In hydrated systems, these metals are mobilized due to the low pH of the system. Cd forms carbonates and hydroxycarbonates [5,10,40]. Ni and Co can replace Ca in calcium silicate hydrate [5,10], although some authors have reported positive results for Ni, due to the presence of part of the metals as carbonates [38]. In non-hydrated systems, carbonation may increase the leaching of Ni due to the lower pH of the system (pH = 7–8.5); however, at a field scale trial, it was reduced significantly [22]. |
| Ba | The leaching is much lower in carbonated samples due to its insolubilisation through the formation of $BaCO_3$ and $BaSO_4$, and the decomposition of ettringite [1,38]. |
| Cr | In hydrated systems, this metal substitutes for silicon and chemically incorporates into C–S–H [10]. In some cases, its leachability is increased by carbonation due to the pH decrease and polymerisation of C–S–H, but its concentration is below the set limits [41]. In non-hydrated systems, leaching has been seen to decrease as a result of the formation of calcite, the modification of the pore structure and the precipitation of double salts containing toxic species due to the high affinity of its oxyanions with respect to the neoformed minerals [39,42]. |
| Hg | Hg remains as an oxide, so it is not well retained [10]. HgO does not react with cement. |
| Sr | The leaching of this element is diminished by carbonation. The metal is more tightly bound through solid solution in calcium carbonate [5]. |
| As | This metal is not well retained in carbonated samples, unless pre-treated first [2,40]. |
| NO_3^- | These ions are rapidly released, revealing the physical changes occurring in the carbonated waste form [2,5]. |
| Cl^- | These ions are only partially immobilised, mainly due to the decomposition of Friedel's salt [1,2,41]. |
| SO_4^{2-} | Their concentration in the leachates is below the limits, even though their leaching is increased due to the decomposition of ettringite [2,41]. |

carried out on process waste from soap manufacture (known as Galligu) [45]. The treated product was a granular aggregate, which could be used on the site as engineering fill, as it met Highways Agency specifications once treated. In

addition, the immobilisation of contaminants or leaching properties in Galligu were improved, allowing the treated material to be used in contact with ground water [46]. This followed the earlier trials on contaminated land in Dartford

Table 7
Methods of carbonation and their main features

| Method | Main feature |
|--|--|
| Carbonation with dry CO_2 under pressure | The solid samples are dehydrated by the flowing of the dry gas, causing water starvation in the carbonation reaction. |
| Carbonation in static and dynamic systems at low pressures | The heat released by the reaction vapourizes a portion of the water present within the solid. In the dynamic system, the constant flow of CO_2 helps to remove this water vapour, while in the static system, the water vapour is trapped and can saturate the CO_2 atmosphere [9]. |
| Vacuum carbonation | This is carried out at near vacuum pressures in the presence of a desiccant [2]. These conditions diminish the resistance of water transport from the carbonating solid to the desiccant due to the large average free space left for the water vapour molecules. This method has been shown to give more complete carbonation. |
| Carbonation at high pressure | At elevated pressures, larger amounts of gas are introduced throughout the sample before pore closure occurs, so carbonation is enhanced [9]. |
| Supercritical carbonation | The gas in these conditions increases the reactive inner surface of the cementitious solid microstructure, by dissolving the pore water content and replacing the structurally bound water of $Ca(OH)_2$ and C–S–H with CO_2 [43]. The $scCO_2$ behaves like a dense gas, acting as a solvent for water [43], but exhibits no surface tension, allowing penetration into very fine pores. The result is a product with enhanced mechanical properties, and a considerable morphological change [44]. |

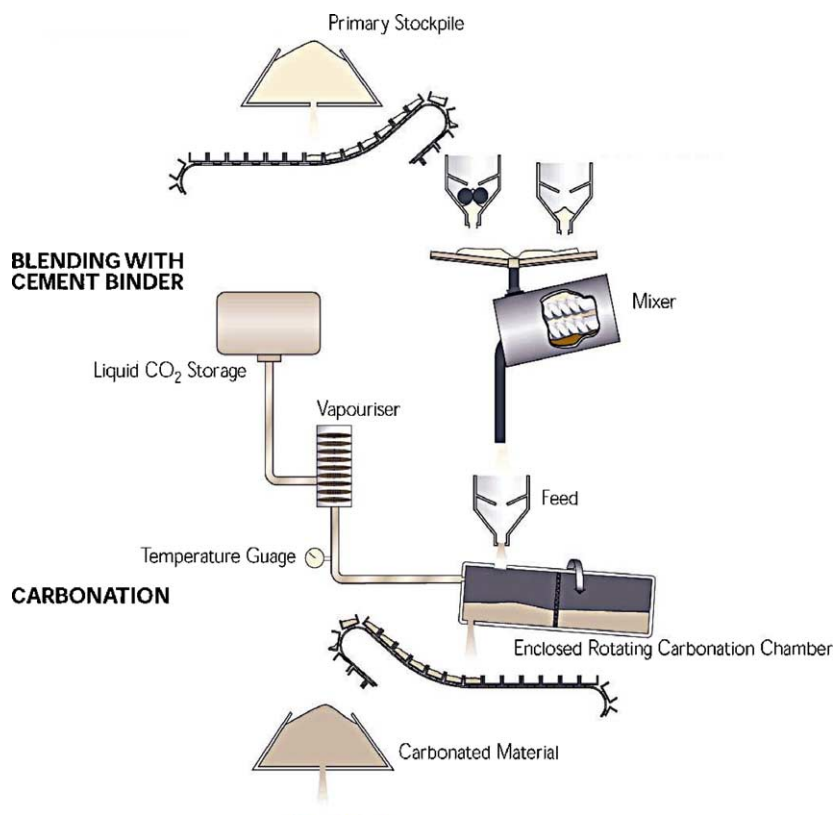


Fig. 7. Schematic of an accelerated carbonation process (courtesy of Forkers).

where more than 99% of the heavy metals present in the soil were immobilised [47] and leachates were able to meet drinking water standards for the metals of concern. Fig. 7 shows the experimental batch process used in this site trial. It shows separate mixing and carbonation chambers, whereas a combined mix and carbonation process is currently being used. This process has been further developed, and is now available as a continuous process capable of a 50 t/h throughput [48].

Other authors have considered the possibility of carrying out *direct carbonation* in a rotary kiln-type operation, or a fluidised bed process. Process heat integration is required so that there is heat exchange between the hot reaction products and the cold reactants. This is considered to be the best method if the raw materials react quickly with CO₂ at elevated temperature. However, the need of working at high pressure can raise the costs of the process significantly [49].

6. Conclusions

The effects of carbonation on the properties of cementitious materials are different. Despite the known adverse effect in some systems, in many cases, the outcome may be beneficial.

- There is a great potential applicability of carbonation technology, not only to stabilise a vast range of waste

materials, but also to generate products with specific physical and chemical properties.

- To be susceptible of carbonation, the materials must be inorganic in nature, containing calcium and/or silicon salts. They may be hydraulic, pozzolanic, lime-bearing or other CO₂-reactive calcium-containing material with heavy metals.
- Greater carbonation is achieved when the solid has high concentration of CaO, and presents a high surface area. As regards the exposure conditions, the carbonation is optimum when the relative humidity is kept at 50–70% and the pressure is slightly positive.
- After the treatment, the contaminants, namely heavy metals, are either absorbed or insolubilised, or physically encapsulated. Carbonation could have either a beneficial or deleterious effect on (trace) element mobility in cement-based systems, which seems dependent on the type of waste, and the type and severity of the CO₂ treatment.
- The strength developed in a carbonated solid can be up to 45% higher than that developed when cured in N₂ atmosphere.
- Some waste materials have consumed more than 50% CO₂ w/w, which indicates the great potential for the utilisation of CO₂ emissions.

There is a growing interest in the potential of accelerated carbonation technology because it has been demonstrated

that contaminated solids of cementitious nature can be rapidly re-mediated whilst binding significant quantities of CO₂. Therefore, accelerated carbonation provides a way of sequestering CO₂ as a solid salt in a variety of treated products reducing landfill waste volumes.

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