Homogeneous Catalysis of the Accelerated Carbonation of Portland Cement

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Abstract

A mechanism proposed for the accelerated carbonation of Portland cement has shown how the reaction proceeds through gaseous, liquid and solid phases in 9 distinct sequential steps. The overall speed of reaction is thus determined by the slowest step, and we have found that solvation and hydration of CO_2 in water is commonly the rate-limiting step in the carbonation process. The literature suggests that the speed of this step might possibly be increased by three different classes of chemical 'enhancers' of CO_2 hydration: (1) inorganic oxy-anions such as hypochlorite (ClO^-) or sulphite (SO_3^{2-}) which act as Lewis bases to CO_2; (2) organic solutes which form anions at alkaline pH, such as sugars and polyhydric alcohols; or (3) amines and alkanolamines, which may exert catalytic action by producing carbamates with CO_2 by either zwitterion formation or charge-transfer. This paper explores these options in detail, supporting theoretical predictions with precise measurement of the rate of CO_2 uptake in a 'eudiometer', to determine whether such rates might be beneficially enhanced in the carbonation of hydraulic binders and wastes, or in CO_2 capture by mineral sequestration.

Sequential Process Model

During research undertaken in the early 1980s on the accelerated carbonation of fresh Portland cement mortar by gaseous CO_2, precise measurements were made of the uptake of CO_2 gas by means of a specially-designed 'eudiometer'.[1] This work enabled a step-wise model to be developed which describes and explains many characteristics of the process.[2]

The model elucidates qualitatively (and often quantitatively) many of the various phenomena observed in the carbonation process, which consists of nine distinct stages in gaseous, liquid and solid phases, summarised in Table 1.

The sequential nature of the whole process is emphasised in the model, so that the overall speed of reaction is consequently determined by the slowest step. This suggests that if other stages in the reaction sequence were optimised, then solvation and hydration of CO_2 in water (steps 3 and 4) could become the rate-limiting step in the carbonation process.

It is consequently of value to consider how these two steps can be speeded up, in particular by chemical catalysis.

Table 1. Sequence of steps in the accelerated carbonation of Portland cement

No	STEP	DESCRIPTION
1	Diffusion of CO_2 in air	Mixing air with CO_2 decelerates carbonation very considerably.
2	Permeation of CO_2 through concrete	Fresh mortar must be permeable to gas, and a simple component volume model can demonstrate the effect on the rate of carbonation of varying the composition.
3	Solvation of CO_2(g) to CO_2(aq)	Boundary layer transfer is favoured by a high internal surface area of mortar, which can be obtained, for example, by using 'ideal-packed' aggregates.
4	Hydration of CO_2(aq) to H_2CO_3	This is a slow and usually rate-determining step. The solvation and hydration of CO_2 are important in biological respiration and in chemical manufacturing processes, and have therefore been extensively studied.
5	Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}	This takes place almost instantaneously, lowering the pH locally by 3 or more units.
6	Dissolution of cement phases	Because the process is cyclic, this step is both rapid and extensive. About 25% of the cement reacts within a few minutes, generating an appreciable exotherm.
7	Nucleation of $CaCO_3$, C-S-H	The 'induction time' (the interval until reaction begins) is greatly prolonged at low temperatures. Finely divided materials can speed up carbonation by acting as heterogeneous nuclei.
8	Precipitation of solid phases	Depending on humidity and temperature, vaterite or aragonite may form initially, these metastable polymorphs of calcium carbonate eventually reverting to calcite. Moreover, not all the $CaCO_3$ appears as crystalline material.
9	Secondary carbonation	C-S-H gel forms as the result of normal hydration, and may then be progressively decalcified, converting ultimately to 'S-H' and $CaCO_3$.

## Catalysis of the Hydration of CO_2

Homogeneous catalysis

CO_2/H_2O equilibria are important in many industrial and biological processes, and have therefore been extensively studied. The early literature[3,4,5] showed that simple, mostly inorganic, anions such as hypochlorite (ClO^-) or sulfite (SO_3^{2-}) can catalyse or accelerate the hydration of CO_2, represented in the alkaline conditions of cement paste by the reaction:

$$CO_2 + OH^- \leftrightarrows HCO_3^- \tag{1}$$

Many potential catalyst candidates cited in more recent literature can be ruled out for practical use on grounds of toxicity and/or cost, including arsenite and some of the more obscure organic compounds. It is often difficult to make direct comparisons of catalytic effects, because of widely varying experimental methods and conditions, especially pH. The highest pH investigated has generally been a carbonate/bicarbonate buffer at pH 9.6, whereas in a fresh cement system it will generally be 3 to 4 units higher (i.e. 1,000 to 10,000 times more alkaline).

Sharma & Danckwerts[4] observed that anions with a negative charge localised on a single oxygen atom are strong catalysts, and they fitted well the so-called 'Brønsted relationship', i.e. a linear plot of log[catalytic constant] vs. pKa. However, Dennard & Williams[5] were unable to confirm this relationship, concluding that oxy-anions of non-metals in lower oxidation states with at least one lone pair of electrons (such as SO_3^{2-}, AsO^{2-}, ClO^-, and $BrO-$) are the best catalysts.

For the majority of cases, the nucleophilicity and ability of the anion XO^- to act as a leaving group are paramount and consistent with the mechanism shown in Reactions (2) and (3).

(2)

(3)
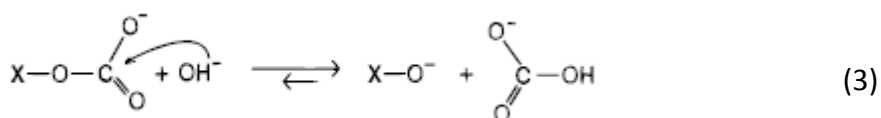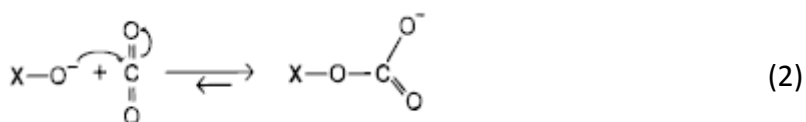
It is now generally accepted[6] that in aqueous solution these species, or their hydration or dissociation products, act as homogeneous catalysts (i.e. dissolved in the liquid phase) whose reaction with CO_2 is followed by a process in which HCO_3^- is released as the catalyst is regenerated (Reaction 3). All of these species feature O^- or OH groups, all can act as Lewis bases for CO_2 (some through atoms with electron lone pairs), and all have a pyramidal or tetrahedral structure (or tetrahedral carbon units) facilitating the approach of the CO_2 molecule to the basic site.

Other Classes of Catalysts
The literature suggests that there may be two further classes of chemical 'enhancers' of CO_2 hydration distinct from the homogeneous catalysts discussed above. Firstly, amine and alkanolamine solutions are frequently used as solvent for the removal of acid compounds from industrial gases. Whereas primary and secondary amines seem to exert catalytic action by producing carbamates with CO_2 by either a 2-stage zwitterion formation or a charge-transfer mechanism, the reaction between CO_2 and tertiary amines can be described by base catalysis of CO_2 hydration.[7,8]

Secondly, organic solutes such as sugars (glucose, fructose, sucrose, saccharose) and mono- and polyhydric alcohols, which form anions at alkaline pH,[4,6] act as catalysts although not as strongly as some inorganic anions.

Vazquez et al.[6] postulated that, assuming Reaction (2) to be the rate-controlling step, it is possible that the catalysis may be facilitated not only by the acidity of the active species but also by its ability to capture CO_2 molecules via polar interactions, which would increase the probability of encounter. If so, the catalytic constant (k_{cat}) should <u>increase</u> with the degree of dissociation of the solute but <u>decrease</u> with the OH density of the solute molecule.

Vazquez did indeed find a correlation between calculated and experimentally determined values of k_{cat} at the buffer pH of 9.6 for various sugars and alcohols studied as solutes, with a 'very good' (though not quantified) fit to the empirical relationship:

$$k_{cat} = 9.83 \cdot \delta^{0.35} \cdot \beta^{-3.95} \tag{4}$$

where $\delta = K_a/(K_a + [H^+])$ = the degree of dissociation of the solute,
$\quad\quad\quad \beta = N_{OH} \cdot m/M$ = the OH density of the solute molecule,
$\quad\quad\quad K_a$ = acidity constant ($kmol/m^3$),
$\quad\quad\quad N_{OH}$ = the number of O^- or OH groups per solute molecule,
$\quad\quad\quad m$ = molecular mass of the OH group (kg/kmol),
$\quad\quad\quad M$ = molecular mass of the solute (kg/kmol).

The fit was also found to be good for arsenite, which suggests that it might apply to other inorganic oxy-anions. Values of k_{cat} have been calculated in Table 2 from Equation (4) at pH 12 (a typical value in fresh cement paste) in ascending order for three classes of catalyst: inorganic oxy-anions, polyhydric organic solutes, and alkanolamines.

It should be noted that this correlation might not be strictly valid at pH values higher than 9.6, and that the nature of the 'O⁻' or 'OH' group has been interpreted rather loosely. Nevertheless, the values of k_{cat} in this Table were used to suggest which additives might be worth investigating in an experimental programme as potential catalysts, bearing in mind issues of toxicity and cost.

Experimental Support

Experimental Programme
Any catalytic effect seems more likely to manifest itself as a speeding up of the maximum rate of carbonation rather than increasing the cumulative CO_2 uptake, although both enhancements might occur simultaneously. Because of this, it is preferable to make measurements continuously rather than to choose two or three fixed times at which to halt the reaction and measure CO_2 uptake in some way, as this may not reveal the true nature of the process.

Experiments carried out previously in the eudiometer (an apparatus which enables very precise measurements of the progressive uptake of CO_2 gas to be taken, described in detail elsewhere[1]) had shown that hypochlorite ion (ClO^-) did indeed appear to speed up the maximum rate of carbonation of sand/cement mortars by a factor of 4 or more, although making little difference to the cumulative CO_2 uptake.[2]

Table 2. Values of k_{cat} re-calculated from Equation (4) at pH 12 for three classes of catalyst: inorganic oxy-anions, polyhydric organic solutes, and alkanolamines (* species investigated by Vazquez et al.[6])

Class	Solute/ion	Chemical formula	pKa	N_{OH}	M [kg/kmol]	k_{cat} [m³/(kmol.s)]
INORGANIC OXY-ANIONS	orthophosphate	$H_2PO_4^-$	12.3	3	98	88
	hypochlorite	ClO^-	7.50	1	37	212
	sulfite	SO_3^{2-}	7.20	2	82	318
	nitrite	NO_2^-	3.25	1	47	546
	sulfate	SO_4^{2-}	1.70	2	96	593
	nitrate	NO_3^-	-2.00	1	63	1737
	hypophosphite	$H_2PO_2^-$	6.70	1	66	2087
	metabisulfite	$S_2O_5^{2-}$	4.00	2	190	8796
	sulfamate	$H_2NSO_3^-$	1.00	1	97	9551
POLYHYDRIC ORGANIC SOLUTES	ethanol *	C_2H_5OH	15.98	1	46	20
	glycerol *	$(CH_2OH)_2.CHOH$	13.70	3	92	26
	glucose *	$(H-C=O).(CHOH)_5-H$	12.50	5	180	116
	sucrose *	$(C_6H_{11}O_5)_2-O$	12.35	8	342	249
	formate	HCO_2^-	3.8	1	46	501
	citrate	$C_3H_4OH.3CO_2^-$	6.40	4	192	593
	acetate	$CH_3CO_2^-$	4.76	1	60	1432
ALKANOL-AMINES	triethanolamine	$(HOCH_2CH_2)_3N$	7.76	3	149	679
	monoethanolamine	$HOCH_2CH_2NH_2$	9.50	1	61	1527

This paper describes a continuation of that work to investigate a wider range of additives. Sand : cement (type I Portland): water mixtures, proportioned 3.0 : 1.0 : 0.25 by weight, were mixed in 5 gramme batches. 2 gramme portions were then compacted by hand (at a pressure of 0.5 MPa) into a disposable 10 mL syringe (14 mm in diameter). The syringe was connected to the eudiometer and the take-up of CO_2 followed for up to 30 minutes. The amount of CO_2 gas reacting as a percentage by weight of cement is calculated from the volume consumed, allowing for variations in ambient conditions (pressure between 1000 and 1020 mbar, temperature between 19 and 22 °C).

Experimental Results

A typical output trace for plain mortar (without any added catalyst) is shown in Figure 1. After an initial delay (an 'induction period' which can be prolonged at temperatures lower than about 15 °C) the uptake rises to a maximum ('R_{max}') before falling asymptotically to a low level. As the maximum theoretical uptake of CO_2 calculated by the Steinour formula for Portland cements is typically in the region of 50%[9], this trace demonstrates that a high degree of carbonation occurs within the first few minutes. The maximum extent of CO_2 uptake achieved in these runs after 24 hours carbonation is of the order of 25% - i.e. about half the theoretical maximum.

Potential catalysts which are commonly available and non-toxic from all three classes listed in Table 2 were tested at a concentration of 500 mM (kmol/m³) in the mortar mix water, a typical level used by previous investigators. Results are summarised in

Table 3, which lists R_{max} (the maximum rate of CO_2 uptake by weight of cement per minute, in % CO_2 $^w/_w$ cement per minute) and the time taken (in seconds) for the CO_2 uptake to reach a given percentage by weight of cement. The control data (plain mortar, no addtive) is the mean of 15 runs undertaken throughout the course of experimentation.
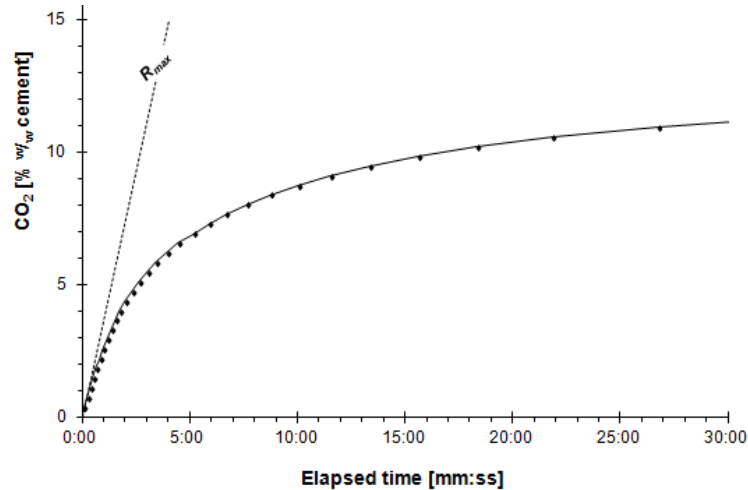

Figure 1. Typical eudiometer output for plain mortar (no additive)

Table 3. Experimental summary: data indicating enhancement of carbonation rates highlighted

Additive @ 500mM	R_{max}	Time (s) to uptake CO_2 (% w/w cement)			
		2%	4%	6%	8%
CONTROL (none)	2.7	53	126	245	543
orthophosphate	0.8	172	363	607	970
hypochlorite	12.4	20	32	107	825
sulfite	1.7	154	290	370	460
nitrite	2.9	39	94	188	357
sulfate	2.6	55	108	173	280
nitrate	3.5	32	74	159	211
hypophosphite	1.6	158	249	326	436
metabisulfite	2.2	186	325	450	648
sulfamate	2.0	61	135	262	521
ethanol	2.4	51	103	169	292
glycerol	1.7	105	178	278	459
glucose	1.9	165	239	319	457
sucrose	1.2	215	333	455	655
formate	2.4	45	95	157	265
citrate	1.9	71	524	862	1324
acetate	2.4	50	103	190	336
triethanolamine	1.6	92	174	274	450
monoethanolamine	1.0	200	613	804	951

These results are somewhat disappointing, as the only additive to give a truly enhanced rate of carbonation was hypochlorite, as shown in Figure 2, though the initial fast reaction with CO_2 seemed to inhibit later uptake. Moreover, this enhancement was observed only when using a freshly prepared solution.
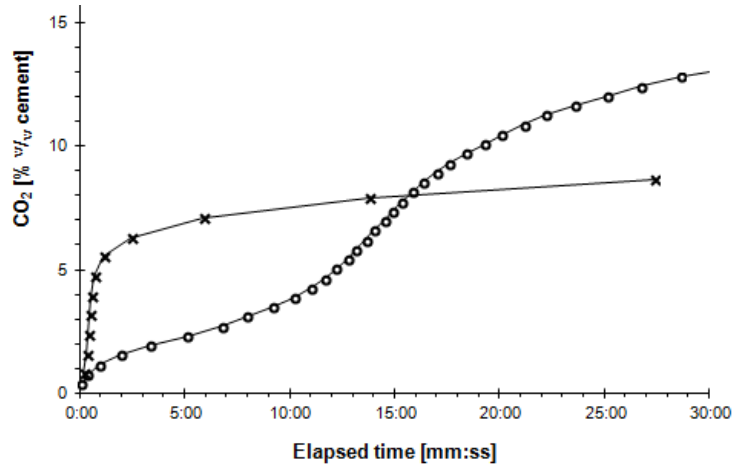

Figure 2. Eudiometer outputs for mortar containing 500 mM calcium hypochlorite (**-x-x-**) and 500 mM monoethanolamine (**-o-o-**)

However, there was some enhancement of rates in all three categories of additive, though not in the order or to the degree suggested by the Vazquez correlation. Furthermore, some additives such as sulphite or metabisulfite did not show the expected enhancement, while others (orthophosphate, citrate) seemed to retard carbonation.

A delayed action was observed with some additives, particularly with mono- and tri-ethanolamine, following an initial very rapid uptake of CO_2. This suggests a possible influence of pH as increasing absorption of CO_2 in the matrix reduced alkalinity in the specimen (Figure 2).
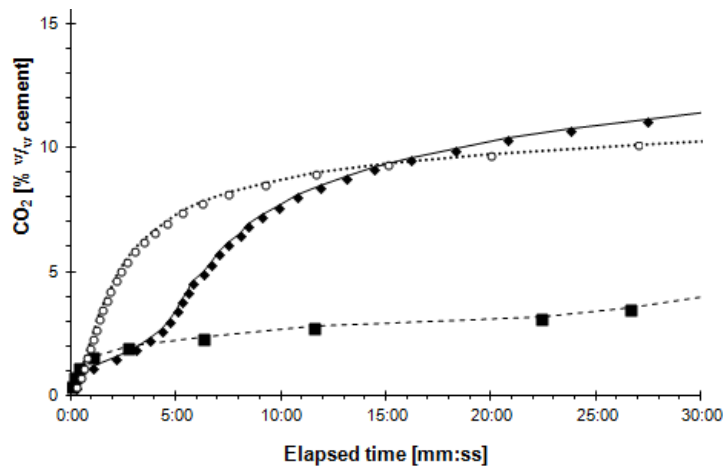

Figure 3. Eudiometer outputs for mortar containing metabisulfite at concentrations of 100 mM (**-o-o-**), 500 mM (**-♦-♦-**) and 2.5 M (**-■-■-**)

But when the concentration of monoethanolamine was raised 5-fold to 5M, the uptake of CO_2 was very fast right at the start, suggesting that CO_2 is absorbed rapidly into the aqueous phase, particularly as uptake continued only slowly thereafter.

The rate-enhancing effect of some additives seems to be concentration dependent, as evidenced by the effect of adding metabisulfite at a concentrations of 100 mM, 500 mM and 2.5 M (Figure 3).

Other additives such as orthophosphate and citrate actually seem to retard the uptake of CO_2, for reasons which are as yet unclear..

Discussion

Experimental results did not turn out to be quite as expected, and they seem to raise more questions than they answer.

Despite the enhancement of CO_2 hydration reported by previous investigators[3,4,5], none of the inorganic oxyanions except for hypochlorite appeared to have any significant effect in these experiments. This may be because the calcium salt used here can react with carbon dioxide to form calcium carbonate and release dichlorine monoxide gas, which would be predicted to have catalytic properties. Furthermore, the hypochlorite ion is a strong conjugate base which would be expected not to hydrolyse at high pH, unlike some other oxyanions.

The delayed action shown by some additives (e.g. monoethanolamine, Figure 3) may due to lowering of pH to a level where the additive is able to enhance the carbonation rate. This may at least partly explain the poor performance, as no data is reported in the literature at a pH higher than that of the carbonate/bicarbonate buffer at pH 9.6. Unfortunately, experiments to test this hypothesis with monoethanolamine using stainless steel slag instead of cement in the mix have so far been inconclusive.

Most of the additives investigated in this work are well known[12] to affect the hydration of cement, aliphatic organic acids being mild retarders (citric more so), saccharides stronger retarders, and inorganic (oxy-) anions mild accelerators. Carbonation is always accompanied by hydration, as the overall stoichiometry of the reaction of CO_2 with silicate phases in cement[10], shown below in (5) for tricalcium silicate, indicates:

$$3CaO.SiO_2 + yH_2O + (3-x)CO_2 \rightarrow xCaO.SiO_2.yH_2O + (3-x)CaCO_3 \qquad (5)$$
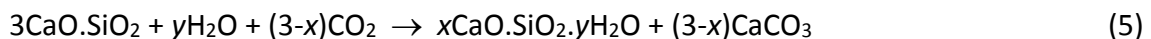
However, those additives which are well-known retarders (such as sucrose and citrate) do not prevent appreciable strength being developed after carbonating for only a few minutes.

Time did not permit an adequate investigation of the effects of varying mix composition, other than to note that changing the w/c ratio had no effect other than slowing down carbonation, by starving the system of water at low values or by blocking ingress of gaseous CO_2 at high values. Nevertheless, varying the concentration of the additive may have significant outcomes as, for instance, raising the level of

metabisulfite 5-fold was found to suppress carbonation, whereas lowering it 5-fold seemed to have the opposite effect (Figure 3).

Conclusions

The relationship suggested by Vazquez[6] for predicting the catalytic effect on CO_2 hydration of additives from a knowledge of their structural chemistry was not confirmed in these experiments. Yet some enhancement of rates was still observed in all three categories of additive, though not in the order or to the degree suggested theoretically.

Tri- and mono-ethanolamines appeared to enhance the absorption of CO_2 into the aqueous phase of the mortar matrix, but did not increase the carbonation rate thereafter. This action might prove useful to aid the initial ingress of CO_2 into an matrix which has an 'unreceptive' microstructure, perhaps too water-saturated or densely packed.

Of the 18 additives investigated, only hypochlorite ion was observed to have a significant rate-enhancing effect, although it is possible that some of the other additives might work better in systems with different chemistry and microstructure. More experimental work is needed to confirm these and other aspects of this study, in particular the effects of varying the concentration of additives and of their action in systems with pH inherently lower than Portland cement. This would be the case with the carbonation of wastes and mineral sequestration, where the matrix is not as alkaline.

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