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Calcium carbonate efflorescence on Portland cement and building materials

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Abstract

Whitish deposits of calcium carbonate, $CaCO_3$, frequently develop on Portland cement concrete and on masonry units, including brick and tile, which have been bonded with Portland cement. These surface deposits are termed efflorescence and are most frequently encountered in new or recent construction. While efflorescence is not normally damaging, except possibly to decorative coatings, it is aesthetically undesirable. The origin of efflorescence is explained and a physicochemical model is developed to explain and quantify the key features of its formation. Calculations and experiments highlight the important role of soluble alkalis in the formation of efflorescence. Mechanistic interpretations and calculations suggest ways in which efflorescence can be mitigated by interrupting one or more steps of the process in conjunction with improved materials selection.

Keywords: Carbonation; $CaCO_3$; Alkalis; Pore solution; Thermodynamic calculations

1. Introduction

Building materials undergo a wide range of physical and chemical reactions in their service environment. Certain of these reactions involve dissolution and physical migration of soluble salts with reprecipitation. When this occurs at depth, within pores in the solid matrix, the phenomenon is termed *subflorescence*. Subflorescence may on occasion be expansive with resulting physical disruption to the physical coherence of the matrix. However, Portland cement and other building materials joined with Portland cement, e.g., brick, are liable to develop surficial deposits termed *efflorescence*. These whitish deposits are not normally expansive but are aesthetically undesirable. They present an irregular mottled appearance, the extent of which fluctuates seasonally, and varies in colouration depending on orientation and position of the construction. These patterns have received much description in the literature, together with speculation as to their causes and prevention; however, we concern ourselves with the underlying mechanisms and the potential for mitigation of efflorescence.

Several papers outline relevant considerations [1–3]. These references suggest, and it is generally accepted that, other factors being equal, increased permeability of the construction results in increased intensity of efflorescence. However, simply reducing permeability is not necessarily a solution: some materials, e.g., clay brick and cement mortar, require a controlled permeability to achieve satisfactory frost resistance and control of moisture movement. Kubayashi and Uno [4,5] correlate increased efflorescence with increased cement alkali, sodium and potassium, contents. They explain that soluble alkalis increases the solubility of $Ca(OH)_2$: this increased solubility, coupled with transport of soluble calcium towards the surface where atmospheric CO_2 was present, is postulated to result in $CaCO_3$ precipitation. This explanation is only partially correct: as will be shown, alkalis present in solution, effectively as NaOH and KOH, actually reduce the solubility of $Ca(OH)_2$. A link with cement alkali contents is, however, firmly established from empirical evidence. It therefore remains to be established why alkalis, which are not themselves constituents of the efflorescent deposits and which reduce the solubility of $Ca(OH)_2$, can promote and enhance efflorescence.

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The present paper develops and evaluates a model for efflorescence. The model is mainly based on physiochemical processes and data described in the literature, although new data were required to evaluate certain of the steps and it has been necessary to integrate the relevant data into an overall model.

2. Processes

In order to describe efflorescence in terms of a physiochemical model it was necessary to consider what features and processes had to be included: the features for a practical model were that it:

- was comprehensive, inasmuch as it could describe calcium carbonate formation under a wide range of conditions relevant to typical exposures;
- was divisible into steps, each of which was capable of a physiochemical evaluation or measurement but which, overall, corresponded with reality and reproduced the observed phenomena; and
- gave insight into possible ways of mitigating or eliminating efflorescence.

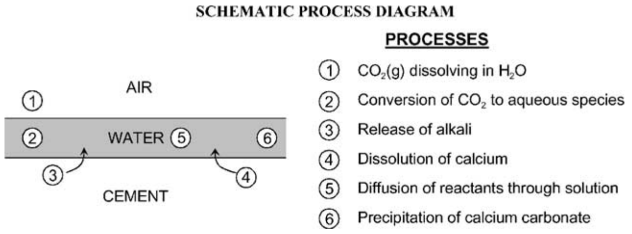

Fig. 2. Schematic process diagram for the formation of efflorescence. Single arrow shows movement of chemical species across interfaces and the double arrow, movement of species within the liquid layer.

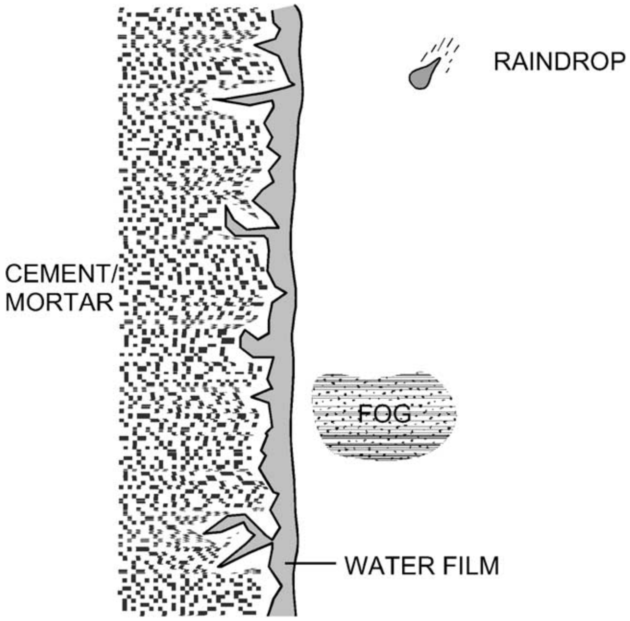

Fig. 1. Schematic view of the macroscopically and microscopically rough surface of a cement, mortar or concrete surface, showing near-surface irregularities. Rain and fog or other condensates develop a layer of water at the surface. This layer may be discontinuous and is prone to thickening, thinning (as occurs by evaporation) or drip. Its maximum thickness is a function of roughness, capillarity and orientation.

Fig. 1 shows how the model, as developed, relates to geometry. It depicts a cement surface in contact with the atmosphere. On account of the roughness of the surface, its geometric surface area is actually less than its real surface but, as will be apparent, once water arrives at the surface and fills pores, differences between the real and geometric surface areas are insignificant. The surface depicted in Fig. 1 is vertical but in practice it may be inclined; horizontal surfaces are not treated in detail. It is an essential feature of the model that a layer of water develops such that air and cement are no longer in direct physical contact across some or all of the surface: the resulting water film mediates reaction. Water arriving at the surface may be in various forms; dew, fog, or rain or some combination. In any event, the water will almost certainly be CO_2 saturated with respect to atmospheric CO_2 pressure and ambient temperature. In the original development of the model, we wished to limit the mass of water arriving at the surface per unit time. This was done by letting water arrive in definite increments; hence, the generic term ‘raindrop model.’ However, it was subsequently discovered that this was a less essential requirement for implementation of the model than at first believed and, in any event, the geometry of two-dimensional films is easier to treat than streamlined drops, so further development concentrated on the point at which individual droplets coalesce to form a film. Nevertheless, the formation of liquid water is essential to initiate and sustain efflorescence.

On horizontal surfaces, the water layer could reach appreciable thickness but we do not treat ponding in any detail. Justification for this is that problem efflorescence occurs mainly on vertical or inclined surfaces, such that the maximum thickness of the water film is limited by capillarity and/or surface roughness and attitude. This means that, typically, the water film will be thin, < 1 mm. However, the exact thickness is not believed to be a critical parameter of the model.

Fig. 2 is geometrically similar to Fig. 1 but concentrates on the processes occurring. The thickness of the water layer is exaggerated, but it is important to note that the system now contains two interfaces: air–“water” and “water”–solid. Henceforth the term “water” will be used for the aqueous phase with the stipulation that it contains dissolved substances. The formation of efflorescence is controlled by six processes. If we assume that water has already moistened the surface, cement substances begin to dissolve at the water–solid interface. The dissolving species are of two types: those with essentially unlimited solubility, relative to the potential of the source to supply and saturate the film, and those whose solubility is limited, i.e., they may react with formation of a sparingly soluble salt or salts. Examples of the first group include sodium and potassium while examples of the second include calcium, aluminium, silicon, etc., of which only calcium is important in the present context; solubilities of aluminium and silicon are in the micromolar range. Processes 3 and 4, which are coupled, will describe the relevant solubilities. As chemical matter supplied from the cement dissolves, Processes 3 and 4, dissolved matter is free to diffuse throughout the thin solution layer, Process 5. We assume that on account of the thinness of the water layer, with the two interfaces typically separated by a distance ranging from a few microns up to a few hundreds of microns, self-diffusion is not in general rate limiting: diffusion occurs principally across the thinnest dimension. Once water is chemically modified by dissolution of cement components, its solvency for CO_2 is also affected. As a result, a new dissolution equilibrium is established which, as will be shown, results in enhanced dissolution of CO_2. CO_2 initially dissolves as molecular CO_2 but depending on composition and pH of the solution, the speciation of CO_2 adjusts to a new equilibrium amongst CO_2 (aqueous), H_2CO_3, $H_2CO_3^-$ and CO_3^{2-} species. These processes are incorporated within Steps 1 and 2. Finally, Ca species from cement and dissolved CO_3^{2-} react, precipitating $CaCO_3$ once its solubility limit is attained. This reaction, including the solubility of $CaCO_3$, is described as Process 6.

These six coupled processes enable the efflorescent cycle to be described and analysed. The analysis, and data underlying its evaluation, will be presented.

3. Implementation and evaluation

3.1. Calculations

In recent decades, a number of computer-based routines have become available for the calculation of thermodynamic equilibria in heterogeneous systems involving solid, aqueous and gas phases. These have as their objective minimisation of the free energy of a defined system, although in some cases, systems partially open to transport of chemical mass can also be evaluated. A recent book [6] describes the basic procedures, including thermodynamic and mathematical procedures, which are employed to converge on numerical solutions. In this study, the computer routine PHREEQE was used [7]; the reference is to the original version although more modern and user-friendly versions have become available since the work was done. The routine comes with a large database of thermodynamic values and various options for correction of solution activities. In most cases, and unless otherwise noted, Pitzer corrections were used to relate activities and concentrations. The computer-based calculations are faster than hand calculations but both rely for their accuracy on the quality of the underlying database. Fortunately, reliable data exist with which to evaluate most reactions although, as is often the case, additional data are required to address kinetic limitations.

3.2. Results

3.2.1. Calculation limits

Several sets of preliminary calculations were performed. To reduce the number of results presented, only calculations for 25 °C are presented although it is easy to perform calculations for other selected temperatures within the normal service environment of building materials and within the range of liquid water. A sensitivity study reveals that temperatures in the range 0–30 °C do not have major impact on the calculations presented here. Total pressure is assumed to be 760 Torr (1 atm) and the partial pressure of CO_2 is assumed to be that of the normal atmosphere, 4 Torr, unless otherwise stated.

3.2.2. Solubility of calcium in NaOH, KOH solutions

The solubility of $Ca(OH)_2$ in mixed NaOH, KOH solutions can be evaluated approximately, without need for a computer-based solution, from the common ion approach. For example the solubility product, K_{sp}, of $Ca(OH)_2$ takes the form:

$$K_{sp} = [Ca][OH]^2$$

where square brackets denote molar concentrations of species. Thus, in initially pure water at 25 °C, $K_{sp} = 42.21 \times 10^{-5}$, and soluble Ca = 21.91 mM (2.19×10^{-2} M).

If $Ca(OH)_2$ is instead dissolved in 0.5 M NaOH, and assuming complete dissociation of NaOH, the calculated Ca solubility decreases to 1.68×10^{-4} m, i.e., 0.17 mM. So the addition of 0.5 M (NaOH, KOH) decreases Ca solubility from ~22 mM in initially pure water, to ~0.17 mM, i.e., more than a hundredfold decrease. Thus, the explanation given by Kubayashi and Uno, that (NaOH, KOH) *increases* Ca solubility is contrary to calculation. In support of this, Table 1 compares solubilities calculated from simple K_{sp}

Table 1
$Ca(OH)_2$ solubility in water and 0.1 m NaOH

(a) Initially pure water, 25 °C	
Ca = 21.91 mM = 2.19×10^{-2} M: $K_{sp} = 4.21 \times 10^{-5}$	
(b) In 0.5 molal NaOH, 25 °C, [Ca] =	
Experimentally determined	9.5×10^{-4} m
Calculated	
From (a)	1.68×10^{-4} m
From Debye–Huckel	1.78×10^{-3} m
From truncated Davies	1.08×10^{-3} m

theory with results of more sophisticated calculations, as well as with experimentally determined solubilities. The more sophisticated calculations substitute activities for concentrations; while this is not strictly necessary for dissolution of $Ca(OH)_2$ in initially pure water, the higher ionic strengths of 0.5 M alkali solutions do result in deviations from ideality. As a result, calculations using activities and a molal scale give somewhat better agreement with experiment than a K_{sp} approach. Nevertheless, the solubility trends are unambiguous: Table 2 shows how the numerical values of $Ca(OH)_2$ solubility decrease with increasing NaOH concentration. As will be shown, dilute alkali solutions, < 0.1 molal, are of most relevance to the present problem and the reduction of solubility of $Ca(OH)_2$ is most marked at low alkali concentration.

3.2.3. Solubility of calcium carbonate in alkali hydroxide

Fig. 3 shows the impact of alkali on $CaCO_3$ solubility. The starting point on the curve represents the solubility of $CaCO_3$ in initially pure water. Very small additions of alkali initially *decrease* $CaCO_3$ solubility, which passes through a minimum at ~0.05 mM, before again increasing. The explanation of the solubility minimum lies in changes in speciation of carbon dioxide as a function of pH. At zero alkali contents, carbon dioxide is speciated mainly as $CO_2(aq)$, H_2CO_3 and HCO_3^-; however as pH is increased by addition of alkali hydroxide, CO_3^{2-} becomes the dominant solution species. The rate of change of aqueous CO_2 speciation perturbs $CaCO_3$ solubilities and is most rapid in the vicinity of this minimum. However, the initial solubility decrease is relatively small and, following the solubility minimum, the gradual increase in solubility with increasing alkali hydroxide concentration is also slight, with the result that $CaCO_3$ solubility in 0.02 millimolal alkali does not much differ from its solubility in pure water.

The calculations were done using molal concentrations but in dilute solutions molal and molar scale are very nearly equal. We will use molar (symbol M) and molal units (symbol m) interchangeably with the reservation that extremely precise calculations may require consistent units. For this reason, units will be given.

Table 2
The solubility of $Ca(OH)_2$ with increasing NaOH concentrations at 25 °C

[NaOH] (mM)	$Ca(OH)_2$ solubility mM
0	21.91
10	18.60
20	15.72
30	13.28
40	11.26
50	9.630
60	8.320
70	7.269
80	6.418
90	5.730
100	5.160
200	2.490
300	1.603
400	1.198
500	0.950

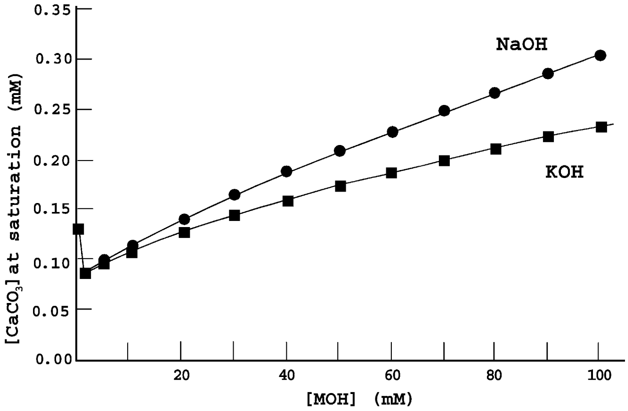

Fig. 3. The effect of alkali hydroxides upon calcium carbonate solubility at 25 °C. The minimum solubility, ~0.8 mM, occurs at MOH concentration ($M = Na^+$, K^+) approximately 2 mM.

At concentrations up to 0.02 millimolal alkali, NaOH and KOH have virtually identical impacts on $CaCO_3$ solubility but thereafter, at higher concentrations, NaOH is calculated to have a somewhat greater impact than KOH at equivalent molalities. Nevertheless, even at 0.1 m NaOH enhancement of $CaCO_3$ solubility, relative to water, is still only a factor of ~3. As will be shown, this is negligible relative to other factors that will be elucidated, notably the enhancement of CO_2 solubility at elevated pH.

3.2.4. Carbon dioxide solubility at elevated pH

The measured solubility of CO_2 in initially pure water, measured at 25 °C and $P_{CO_2} = 4$ Torr (the prevailing partial pressure of the atmosphere) is 1.8×10^{-4} molal. Once CO_2 dissolves in water, which is itself partially ionised:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad (1)$$

The dissolved CO_2 is present as a mixture of species: some as CO_2 (aq), some as “carbonic acid”, H_2CO_3, which itself ionises giving an acidic pH and bicarbonate ions.

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (2)$$

In alkaline solution, such that $[OH^-] >> [H^+]$, the reaction dissociation of bicarbonate occurs:

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O \qquad (3)$$

The extent of self-dissociation is small at self-generated pH. If, however, OH^- ions are added from an external source such as $Ca(OH)_2$, NaOH or KOH (or mixtures thereof) the equilibria are displaced and CO_3^{2-} becomes the principal aqueous species. For example, in dilute alkali, using NaOH as an example, the products are best represented by Eqs. (4) and (5):

$$2\mathrm{NaOH(aq)} + \mathrm{CO_2(aq)} \rightleftharpoons 2\mathrm{Na^+(aq)} + \mathrm{CO_3^{2-}(aq)} + \mathrm{H_2O} \tag{4}$$

and

$$2\mathrm{Na(aq)^+} + \mathrm{CO_3^{2-}(aq)} + \mathrm{CO_2(aq)} \rightleftharpoons 2\mathrm{Na^+(aq)} + \mathrm{HCO_3^-(aq)} \tag{5}$$

Thus the CO_2 solubility at a particular temperature and CO_2 pressure is approximately proportional either to $[\mathrm{OH}]^2$ or $[\mathrm{Na}^+/2]$. Corresponding equations can be written for K. The mixture of species comprises a buffered system, the pH of which will be calculated subsequently.

The consequences of the impact of NaOH or KOH on CO_2 solubility are depicted in Fig. 4. While CO_2 solubility in pure water is low, ca. 1.8×10^{-4} m at 25 °C, in 0.1 m NaOH it increases to 0.071 m, a factor of nearly 400. The extreme sensitivity of CO_2 solubility to alkali hydroxide concentration, particularly at low (<0.1 m) concentrations, is a key parameter in the formation of efflorescence as it enables the aqueous phase to dissolve and potentially store CO_2. The additional increase in solubility of CO_2, by orders of magnitude relative to self-generated solubilities, vastly increases the potential of the solution to absorb atmospheric CO_2.

Because a carbonate–bicarbonate equilibrium is operative, the pH of a (Na, K)OH solution containing dissolved CO_2 is reduced relative to the pH of a corresponding (Na, K)OH solution in water. Harte et al. [8,9] developed the semiempirical equation shown in Eq. (6) for calculation of pH. Where X is the mole fraction sodium as $NaHCO_3$, C the total Na concentration, S the solubility of CO_2, P the partial pressure of CO_2, T= temperature °C and $(1-x)$ the mole fraction Na present effectively as carbonate is given by:

$$X^2 \times C^{1.29}/S \times P(1-x) \times (185-T) = 10 \tag{6}$$

Table 3 shows the pH calculated from Eq. (6). At first the pH increases rapidly, reaching 10.2 at 0.1 molal NaOH, but thereafter increasing only slowly as the NaOH concentration increases.

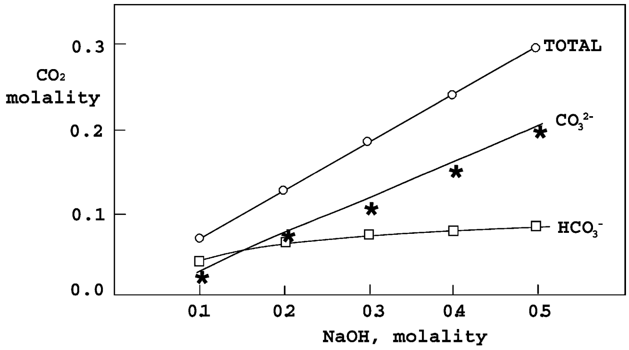

Fig. 4. Solubility of HCO_3^-, CO_3^{2-} and total CO_2 (all species) in the aqueous phase as a function of Na OH. The data assume P_{CO_2} is 4 Torr and temperature 25 °C. On this scale, the solubility of CO_2 in pure water is near zero.

Table 3
pH of NaOH solutions saturated at $P_{CO_2} = 3 \times 10^{-4}$ Torr, 25 °C

NaOH molality	pH
0.01	9.32
0.1	10.21
0.2	10.45
0.3	10.57
0.4	10.65
0.5	10.71

Dissolved $Ca(OH)_2$, on the other hand, cannot sustain corresponding increases in CO_2 solubility because of the relative insolubility of $CaCO_3$; precipitation removes carbonate ions.

3.2.5. Absorption of CO_2 at the air interface

Absorption at the air interface is a complex phenomena. For example, if the gas phase at the air–water interface is stagnant it may become locally depleted in CO_2. Fortunately, zero air flow is almost unknown in outdoor conditions, thereby enabling this condition to be dispensed with. Moreover, the thin liquid films responsible for driving efflorescence imply that diffusion in the liquid film is not likely to be rate limiting: self-diffusion of simple, low-mass ions is sufficiently rapid to maintain transport. It is, however, well known that the rate of CO_2 sorption of CO_2 into pure water, Process 1 in Fig. 1, is slow because of the slow reaction of CO_2(aq) to form H_2CO_3. However in alkaline solutions, such that the abundance of OH^- is increased by orders of magnitude relative to pure water, hydrolysis of CO_2 is rapid and dissolution of CO_2 is similarly enhanced. Under laboratory conditions, the presence of alkali hydroxide accelerates the CO_2 sorption reaction: indeed, "the relative rate of sorption of CO_2 by 0.2 M KOH at 30 °C is 10 times more rapid than the sorption of carbon dioxide by initially pure water at 30 °C" [10]. In this respect, some differences occur between NaOH and KOH; the latter absorbs CO_2 more than twice as fast as NaOH of corresponding molarity, at least up to 3.5 M KOH [11]. At the same time, the viscosity of a KOH solution is lower than that of a NaOH solution of identical concentration and this additionally accelerates transport in the solution. However, the model does not need precise numerical data on CO_2 absorption kinetics provided it is assured that this step is not rate limiting: data in the literature afford the necessary assurance.

3.2.6. Leachability of alkalis

The importance of alkali to the workings of the efflorescent process has been emphasised. The principle source of alkali is of course the cement itself. The leachability of alkali from cement is a factor that cannot be calculated but has to be determined experimentally. We were unable to find

Table 4
Representative leaching of alkali from hardened cement paste

Time, min	Leach rate, mol/min/cm^2 at 25 °C		
	Sodium (Na)	Potassium (K)	Calcium (Ca)
10	9.903×10^{-9}	2.761×10^{-8}	8.799×10^{-8}
30	2.625×10^{-9}	2.918×10^{-8}	1.090×10^{-8}
60	1.484×10^{-9}	1.071×10^{-8}	2.920×10^{-8}
180	5.428×10^{-10}	3.806×10^{-9}	1.332×10^{-8}
360	4.948×10^{-10}	3.353×10^{-9}	9.336×10^{-9}
Mean	3.01×10^{-9}	1.43×10^{-8}	3.02×10^{-8}

appropriate data in the literature, so undertook to determine data with which to evaluate the model. An ordinary Portland cement conforming to ASTM Type I specification was selected. By chemical analysis, this cement was found to contain 0.55 K_2O and 0.07 Na_2O (as weight percent of anhydrous cement). The cement was mixed to w/c = 0.43 and cast into jacketed cylinders 42 mm in diameter. These were cured at 98% r.h. for 28 days at 55°, taking precautions to minimise carbonation and water loss by additional confinement by sealing the cement into plastic bags to which a few drops of water had been added. After cure, one flat face was exposed to 250 ml of distilled water for 10, 30, 60, 180 and 360 min: CO_2 was excluded and the solution analysed for dissolved alkali by flame photometry. The intrinsic leach rates, normalised to moles per minute per square centimeter, are presented in Table 4. The initial leach rate of sodium and calcium show spikes but thereafter, leach rates tend to become more regular and decline, albeit slowly, after 180 min. For calculations, we use averaged alkali release values. Thus, for example, if averaged alkali release rates are assumed to dissolve into a water film 0.1 mm thick, the film achieves 0.01 M KOH in about 15 min. The calculation is illustrative, showing how easily a fresh cement can rapidly condition a thin film of water to relatively high alkali contents, on the order of 10^{-2} to 10^{-1} molal.

4. Discussion

4.1. Workings of the efflorescent cycle

The workings of the efflorescence cycle can now be explored in more detail. When moisture appears at the surface of cement, it dissolves cement substance. Even traces of alkali, effectively present as NaOH and KOH, increase the pH of water drops or films. As the alkali aqueous contents increase, its solvent power for CO_2 increases. The extent of the solubility increase required for CO_2 saturation is remarkable; typically several hundredfold relative to pure water. Moreover, the kinetics of sorption of CO_2 at the air–water interface are also accelerated; the presence of enhanced hydroxyl ion concentrations catalyses the reaction of dissolved CO_2, to yield HCO_3^- and CO_3^{2-} species: progressive removal of CO_2(aq) facilitates continued dissolution of gaseous CO_2. Thus, as $CaCO_3$ is precipitated, a ripple of displaced reactions occurs in order to maintain a gas–solution equilibrium. As noted, the significance of a potential rate-limiting step, of the conversion of dissolved CO_2 to H_2CO_3, is reduced by increase in alkalinity. However, the greatly increased carbonate content also limits the rise in pH, which typically will be buffered in the pH range 9.5–10.2, the exact pH depending on aqueous chemistry; principal dissolved carbonate species are thus CO_3^{2-} and HCO^{3-}.

Sensitivity studies disclose that the buffering action, achieving pH close to 10 and not exceeding 11, is achieved over a wide range of conditions (temperature, alkali concentration, nature of the alkali—sodium, potassium, or mixtures of the two—and of different water film geometries). This means that the example calculations and mechanisms developed here will be broadly applicable to different types of construction and exposures, as well as to different cement types as well as mortar and concrete formulations, etc.

The reaction mechanisms are also constant, or nearly so, across a wide range of constructions. Once a moisture film is established, spatially separated sets of coupled chemical reactions are initiated. These are driven by transport across two interfaces, air–water and water–solid, as well as by transport within the "water" itself. As water dissolves cement alkali, it becomes undersaturated in CO_2 (all species), typically by two to three orders of magnitude relative to pure water. The speciation of CO_2 occurs increasingly as carbonate, CO_3^{2-}, as it diffuses towards the cement–aqueous phase contact where, upon meeting Ca ions, either in solution or migrating through pores in the cement paste, $CaCO_3$ precipitates. The solubility of $CaCO_3$ is low at all pH values in the buffering range. The favoured site for precipitation is close to the source of Ca ions, i.e., the water–cement interface. As precipitation of $CaCO_3$ progresses, it covers the cement surface so that continued transport of ions from the cement paste must increasingly occur through a surficial $CaCO_3$ deposit.

An important feature of the model is that alkali is not removed from solution in the precipitated product, $CaCO_3$. Hence, its role is simply to (i) enhance the solubility of CO_2 in the aqueous phase, typically by two or three orders of magnitude relative to its solubility in initially pure water; (ii) enhance the rate at which CO_2 is sorbed into the aqueous phase at the air–"water" interface, typically by an order of magnitude relative to pure water; and (iii) catalyse the conversion of aqueous CO_2 to H_2CO_3, which then rapidly equilibrates with OH^- ions. These three actions reinforce each other with the result that even small amounts of alkali dissolving in the aqueous film are extremely effective in promoting calcium carbonate efflorescence. Dissolved calcium can also increase pH but, unlike sodium and potassium, calcium is rapidly precipitated and cannot maintain sufficient solubility to achieve the same pH impact as alkali.

The peculiar mottled appearance of efflorescence is explained by a combination of three features and processes. The first is the distribution of liquid water at the surface which, on account of surface roughness, joints, cracks, gaps and orientation, e.g., overhangs, may vary from place to place even over short distances. The second factor is the length of time the liquid water persists: since the cycle is self-perpetuating, the amount of efflorescence is also a function of time.

4.2. Extensions to other geometries, chemistries and exposures

Several other factors not directly considered in the model may have relevance. These are considered briefly.

- *Ponding*. In relatively thick layers of water, as may occur on horizontal surfaces, transport of ions through solution becomes rate limiting. Transport in solution occurs by a mixture of flow, self-diffusion, convection and advection. Owing to potentially large changes in transportation mechanisms and kinetics this geometry has not been treated.
- *Other soluble species*. The influence of other potential soluble species on the efflorescent process has been subject to scoping analysis. Chlorides are normally not present in significant quantities in building materials but may arrive with moisture, for example as marine spray. However, the source of chlorides is not crucial to the analysis. Low concentrations of chlorides do not reduce significantly the alkalinity of NaOH and KOH solutions nor much affect their pH buffering action, and hence CO_2 solubilities remain essentially unchanged with respect to the chloride-free system. Therefore the general considerations developed here remain valid when [OH]>[Cl].
- Sulfates are also normally present in cements and may be liberated from brick or stone. During the early life of hardened cement paste, before carbonation becomes significant, sulfate solubilities may be high for a few hours but within 12–24 h usually decrease to much less than would be predicted from the gypsum saturation threshold [12]. Thus OH^- remains the principal counter-ion that charge balances soluble cations. We have not attempted to analyse the situation after significant carbonation has occurred. These factors would have to be the subject of separate research, to establish the potential for sulfate efflorescence. However, the efflorescent product is likely to be gypsum, $CaSO_4 \cdot 2H_2O$, which is more soluble than $CaCO_3$. Hence, gypsum (or other $CaSO_4$ form) is less likely to give rise to long-lived efflorescence than reactions forming $CaCO_3$.
- *Evaporation*. The efflorescent cycle can be interrupted by loss of liquid film: evaporation, perhaps combined with suction into porous media, is a typical cause of drying. During evaporation, the storage capacity of pure water for CO_2 is sufficiently low that formation of efflorescence by complete evaporation makes negligible contribution to efflorescence relative to steady-state transportation, even in the course of repeated wet–dry cycles. However, as noted previously, the CO_2 storage capacity of the system can be increased by several orders of magnitude even at low (0.01–0.1 m) NaOH or KOH concentrations. As water evaporates, either CO_2 can be lost at the air–water interface or $CaCO_3$ precipitation can occur, or both. Thus evaporation may, depending on availability of $Ca(OH)_2$ or C-S-H cement gel for reaction, precipitate additional $CaCO_3$ in the presence of dissolved alkali. If the efflorescent cycle is interrupted, as by evaporation, it is free to commence again by reestablishment of a water film. However, the precipitated products may, depending on permeability, affect reaction kinetics. The quality of the $CaCO_3$ layer and its ability to isolate cement from further reaction is at present unknown.
- In composite construction, e.g., brick bonded with cement mortar, additional factors may influence the visual appearance of efflorescence. Clay brick may contribute alkali or become saturated by alkaline cement pore fluid, or both. Thus efflorescence frequently appears on masonry at or near its contacts with cement. Furthermore, the visibility of efflorescent deposits depends on thickness as well as particle size and polymorphism of $CaCO_3$, both of which are influenced by light scattering and the colour of the background. Thus, the visibility of an efflorescent deposit, other factors being equal, will be greater on a dark background than on a light-coloured substrate.

4.3. Practical measures for mitigation of efflorescence

The implications for avoiding efflorescence are as follows. Efflorescence is a natural and spontaneous process, driven by an approach to thermodynamic equilibrium. The underlying processes are susceptible to analysis and computer modelling using, for the most part, data available in the literature or estimated in the course of this study. It follows from the foregoing that efflorescence can be mitigated but that total avoidance is difficult. Nevertheless, since very thin films of efflorescent products are transparent or nearly so, any building system should have at least limited tolerance to aesthetic impairment.

Although alkali release rates have been derived from a single cement and complete calculations made for only one set of conditions, $P_{CO_2} = 4$ Torr and 25 °C, it is possible to envisage the impacts of changed conditions from scooping calculations. With regard to cement alkalis, two factors emerge as important: total alkali and the fractional rate at which alkalis are released. Modern processes for cement making, having thermal efficiency as their prime goal, not only increase cement alkalis but concentrate alkali in readily releasable form, e.g., as alkali sulfate condensates on clinker grain surfaces.

Other factors being equal, this is likely to lead to an intense burst of efflorescence, but perhaps of shorter duration, than from cement made by more traditional processes. These factors should be considered in devising a satisfactory standard alkali-release test, which would assist in evaluating the potential of building materials to contribute to efflorescence. If the option exists, a low-alkali cement should be selected in preference to one higher in alkali.

The impact of P_{CO_2} and temperature can be evaluated as follows. Atmospheric CO_2 contents are rising and their impact is inevitably to worsen the efflorescence problem. The solubility of CO_2 increases markedly with decreasing temperatures, so efflorescence is likely to be more severe in cold climates. Global warming, perhaps 1–2 °C in the course of the next century, is insufficient significantly to offset the impact of cold winters, which will continue to affect much of the world's built environment.

4.4. Avoidance and mitigation

The best practical advice to mitigate calcium carbonate efflorescence is therefore as follows:

- Use low-alkali cements. If alkalis cannot be avoided, sodium is preferred to potassium. Alkali contents need to be compared on a mole basis; weight percentages are misleading.
- If possible, devise and agree a test to estimate alkali releases. Quick-release sources of clinker alkali, e.g., $(K, Na)_2SO_4$ should be avoided, so a test should determine both total release as well as rate of release.
- If an alkali sorber can be added to cement, this should improve performance. However, it must be able to act quickly and there is doubt that some blending agents, which are claimed to sorb alkali, e.g., coal combustion fly ash, will work with sufficient rapidity totally to avoid efflorescence. Recent studies of alkali sorptivity may assist in materials selection [13,14].
- Use impermeable mortars, so as to reduce the availability of alkali and decrease the effective thickness per unit time of the alkali-depleted layer.
- Do not use cement mortar to bind components that will themselves liberate soluble alkalis: check the potential of other components to liberate soluble sodium and potassium at pH 10–13 and reject those that give high releases.
- Thoroughly wash exterior surfaces after final set of the cement to dilute and flush away alkalis. Do not, however, use acidic washes that will enhance the permeability of the cement surface and may subsequently worsen the problem.
- Where efflorescence is anticipated avoid if possible dark-coloured materials, e.g., dark brick or tile.
- Extend investigations to sulfate efflorescence.

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