Colloid Electrochemistry of Saturated Cement Paste and Some Properties of Cement Based Materials

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In a cement hydration product-electrolyte system the hydration products are micron-sized charged particles. The principles of colloid electrochemistry predict that in such a system each solid particle is surrounded by a layer of concentrated solution of its counter-ion. The actual concentration of this layer depends on the surface charge and the concentration of the solution away from the particle, i.e., bulk solution. Divalent counter-ions preferentially concentrate around the solid particles. The principles also predict that the intrinsic diffusivity of an ion is proportional to the square root of its concentration in a solution. The literature on the expressed pore solution, ionic diffusivity through cement based materials, the formation factor, alkali-silica reaction, etc., has been examined from the point of view of colloid electrochemistry. Many of the reported but unexplained phenomena could be explained from the principles of colloid electrochemistry. ADVANCED CEMENT BASED MATERIALS 1998, 7, 102–108. *© 1998 Elsevier Science Ltd.*

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Whenever two dissimilar materials are brought together an exchange of electrical charges occurs, the extent of which depends on the materials and their subdivision. The cement hydration products are micron-sized particles and form within an electrolyte solution. It is expected that they will be charged particles and their charged state is evident from their zeta-potentials [1–3]. In this review the colloid electrochemistry of saturated cement paste and its relationships with some properties of cement based materials will be presented. The objective is to initiate a discussion so that the field may be developed and systematized.

The Double Layer and Bulk Solutions

Due to their surface charges the cement hydration products have characteristic surface electrical potentials and counter-ions preferentially accumulate adjacent to their surfaces. These counter-ions cannot be removed without contravening the local electroneutrality. In a saturated paste these counter-ions form a solution richer in the counter-ions than the rest of the aqueous phase. This part of the total free water is known as the double layer solution. The thickness of this double layer solution is about a few tens of Angstroms. Only water can be removed from a double layer solution, either by evaporation or by high pressure, without removing the counter-ions. The rest of the free water forms the bulk solution.

Relationship Between the Compositions of the Double Layer Solution and That of the Bulk Solution

Consider a single, charged hydrated cement particle suspended in an uni-univalent electrolyte solution of concentration *c*. In order to find the difference between two solutions, it is necessary to consider an infinitesimal transfer of ions from one solution to the other [4]. This involves work against both chemical and electrical potentials. Let μ_p and μ_s be the chemical potentials of an ion near the particle and in the solution faraway from the particle, respectively. V_p and V_s are the electrical potentials of the two places, respectively. If *dn* mole of an ion is transferred from the bulk solution to near the particle the total work done in the transfer is:

$$\mu_p dn + V_p F dn - (\mu_s dn + V_s F dn) \tag{1}$$

where *F* is the Faraday constant.

At equilibrium

$$\mu_p dn + V_p F dn = \mu_s dn + V_s F dn. \tag{2}$$

As *dn* is a positive number we have

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$$\mu_p + V_pF = \mu_s + V_sF. \quad (3)$$

Using the usual relationship between the chemical potential and activity of the ion in solution we have:

$$\mu^o + RT\ln a_p + V_pF = \mu^o + RT\ln a_s + V_sF \quad (4)$$

or

$$RT\ln a_p + V_pF = RT\ln a_s + V_sF \quad (5)$$

where μ^o is the chemical potential of the ion in the standard state and *a* is the activity in the solution.

Since V_p is not equal to V_s, a_p will also be different from a_s. In dilute solutions, *a*s could be replaced by *c*s. The quantity ($\mu + VF$) is called "electrochemical potential" by Guggenheim [4]. Equation 5 shows that in a charged particle-electrolyte system it is the "electrochemical potential" (not the chemical potential) of each species that remains constant throughout the system.

In a dilute solution the variation of concentration of an ion with electrical potential is given by the Boltzmann factor $e^{-ze\psi/kT}$ [5]. For the case of a positively charged particle suspended in an electrolyte solution consisting of two kinds of ions of charges, +a and −b:

$$n^- = N_o^- e^{be\psi/kT}$$

and

$$n^+ = N_o^+ e^{-ae\psi/kT} \quad (6)$$

where n^- and n^+ are concentrations of anion and cation, respectively, N_os are the concentrations of negative and positive ions at infinite distance from the charged particle, i.e., in the bulk solution, *k* and *T* are Boltzmann constant and absolute temperature, respectively, and $e\psi$ is the electrical potential, in millivolt, at the point. Two relationships of eq 6 could be used to calculate the concentrations of anion and cation near a charged particle from the composition of the bulk solution. At 25°C *kT* has a value of 25.69 mV. The above relationships could not, however, be used within about 10 Å distance of a charged particle [5]. This breakdown is mainly due to the finite size of ions.

A Few Typical Examples

Surface charges or the surface potentials of the cement hydration products have not yet been measured, although the surface charge on CSH has been estimated [1].

Zeta-potentials of hydrated cement and C_3S particles, suspended in different electrolytes, have been published [1–3]. These values could be used to calculate the anion and cation concentrations at a plane just in front of the plane of zeta-potential (slip-plane), i.e., in the Gouy-Chapman part of the electrical double layer, provided the concentration and the nature of the electrolyte are known. Using more complicated mathematics it is possible to calculate the average concentrations of each type of ion in the diffuse double layer. Unfortunately, however, only a few authors have published analyses of the solutions in which they have suspended their samples in the zeta-potential measurements. Though this lack of information hampers a quantitative evaluation of the results, it does not affect the qualitative inferences about the ionic concentrations at the slip-planes. Table 1 shows the calculated concentrations based on some of the published zeta-potentials.

From an examination of Table 1 the following general conclusions may be drawn.

(a) The ionic concentration at the slip-plane is higher than that in the bulk solution (see the cases of cement in NaOH and NaLG, C_3S in NaLG). This applies both to cement and C_3S suspensions. The actual anionic or cationic concentration at the slip-plane depends on the sign and absolute value of the zeta-potential of the hydration product (see the cases of C_3S in NaLG and cement in NaLG).

In this context the presence of a very small amount of an interfacial active compound may play a very important part.

Gartner et al. [3] reported that an addition of 0.0125% sodium naphthalene sulphonate formaldehyde complex (NSFC) to NaLG solution changed the zeta-potential of C_3S particles from −8 mV to −31 mV. This change in zeta-potential should be accompanied by a change in cation concentration from 0.41 to 1.0 N at the slip-plane, and a change in anionic concentration from 0.22 to 0.1 N. An addition of 0.0125% NSFC would hardly change the bulk concentration of NaLG solution, which is essentially a 0.3 N NaOH solution. More dramatic changes occur with a 0.2% addition of NSFC to LG solution when the zeta-potential of C_3S particles changed form +8 mV to −21 mV [3]. In this case the cationic concentration changed from 0.54*C to 5.1*C, i.e., from an anion rich, cation poor solution to a cation rich anion poor solution. It is not known, however, if this effect of interfacial active agents persists in hardened cement pastes.

(b) It is of interest to note that the double layer solution always contains a certain amount of co-ion.

(c) The zeta-potential is negative in the presence of alkali hydroxide solution and positive in $Ca(OH)_2$ solutions.

In a single electrolyte solution the excess ionic concentrations, over that of the bulk solution, in the double layer solution can be assigned uniquely. The situation is not so simple in the case of a mixed electrolyte solution, especially when the electrolyte contains a divalent ion,

TABLE 1. Calculated ionic concentrations at slip-planes of cement hydration products-electrolyte systems

Solid	Bulk Solution		Observed Zeta-potential (mV)	Calculated Ionic Conc. Near Slip-plane		Prehydration Time (hour)	Ref.
	Nature	Conc.		Cation	Anion		
Cement	NaOH	0.1 N	−29	0.31 N	0.03 N	24	1
C_3S	—	A	+36	A*0.06	—	18	2
C_3S	DOE	B	−6	B*1.59	—	0	3
C_3S	NaLG	0.3 N	−8	0.41 N	0.22 N	0	3
C_3S	LG	C	+8	C*0.54	—	0	3
C_3C	LGC	D	+15	D*0.31	—	0	3
Cement	DOE	E	−6	E*1.59		0	3
Cement	NaLG	0.3 N	−16	0.56 N	0.16 N	0	3
Cement	LG	F	+6	F*0.63	—	0	3
Cement	LGC	H	+23	H*0.17	—	0	3

Abbreviations: A = unknown concentrations, assumed to be A molar with respect to calcium ion; B = in demineralized water, unknown concentration, assumed to be B molar with respect to calcium ion; NaLG = 0.3 N Na_2SO_4 solution in equilibrium with excess lime and gypsum, assumed to be essentially 0.3 N NaOH solution; C = saturated lime-gypsum (LG) solution of unknown composition, assumed to be C molar with respect to calcium ion; D = lime-gypsum-$CaCl_2$ (LGC) solution of unknown composition, assumed to be D molar with respect to calcium ion; E = in demineralized water, unknown concentration, assumed to be E molar with respect to calcium ion; F = lime-gypsum solution of unknown composition, assumed to be F molar with respect to calcium ion; H = lime-gypsum-$CaCl_2$ solution of unknown composition, assumed to be H molar with respect to calcium ion.

e.g., cement pore solution containing both $Ca(OH)_2$ and NaOH. In the latter case the question of the preferential selection of divalent ion, e.g., Ca^{2+} over monovalent ion becomes relevant, i.e., ion selectivity factor has to be taken into consideration. For the montmorillonite-Ca/Na/Cl solution system Ca^{2+} concentration more than 50 times that of Na^+ in the inner side of the double layer has been reported even though the bulk solution had a Na/Ca ratio of 3 [6]. More on this point in the section on ionic diffusion through cement pastes.

A Relationship Between the Intrinsic Diffusivity of an Ion and Its Concentration in Solution

A combination of Nernst diffusion equation for ions and Kholrausch's molar conductivity rule gives the following relationship between the intrinsic diffusivity of an ion and its concentration in a solution:

$$D_i = D_o - A\sqrt{c_i} \tag{7}$$

where D_i and D_o are the diffusivity at a molar concentration of c_i and in infinite dilution, respectively; *A* is a parameter [7]. Equation 7 is strictly valid within the Nernst approximation range of about 0.7 molar solutions. The applicability of eq 7 may be extended by a series expansion technique and diffusion measurements at narrow intervals of concentrations to determine the higher order parameters. Kholrausch's results, however, indicate that above about 3 molar concentration, D_i will decrease very slowly with concentration. Equation 7 is equally valid for bulk and double layer solutions. Equation 7 has been found to be applicable to alkali halide diffusion through homoionic clay plugs [8]. To apply eq 7 to thick sections of cement mortar it has to be averaged over the concentration range across the samples [9]. This gives:

$$D_M(C_o) = \frac{1}{C_o}\int_o^{c_o} D\,dc = \frac{1}{C_o}\int_o^{c_o} (D_o - A\sqrt{C})\,dc$$

$$= D_o - \frac{2}{3}A\sqrt{C_o} \tag{8}$$

where D_M is the measured diffusivity of the ion concerned and C_o is its concentration on the upstream side. Equation 8 fits the recent Cl^- diffusion data of Bigas et al. [10] through cement mortar with a regression coefficient of 0.99.

Relationships Between Colloid Electrochemistry and Some Properties of Saturated Cement Paste

It is now possible to examine the relationships between electrochemical and some other properties of saturated cement pastes.

Expressed Pore Solution

Attention has already been drawn to the facts that double layer solutions are the nearest to and in quasi-equilibrium with the cement particles and cannot be removed without contravening the local electroneutrality. It is thus obvious that only the bulk solutions can be

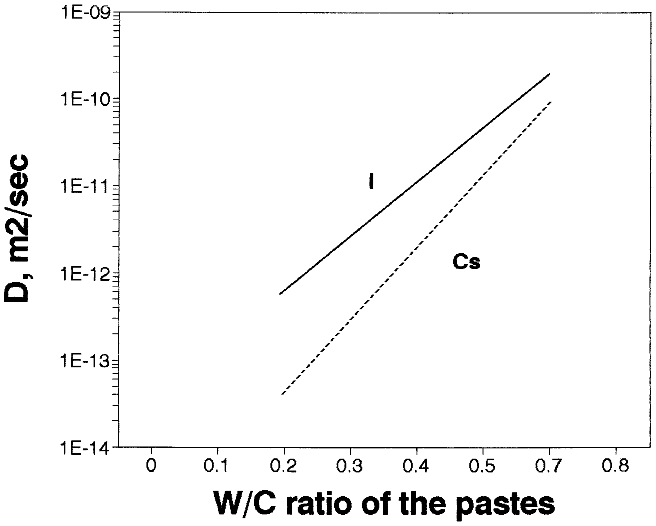

FIGURE 1. Dependence of Cs and I ion diffusivity on the w/c ratios of cement pastes [13].

expressed. At very high pressures or very quick loading pure water from a double layer may be expressed, causing a lowering in the pore solution concentration. This lowering has been reported by Silsbee et al. [11]. Without a knowledge of zeta-potential, the expressed pore solution composition does not allow for a calculation of the composition of the double layer solution and as such is of very little value to evaluate some of the properties of the cement hydration products. More on this aspect in the sections on ionic diffusion through cement paste and the formation factor.

Ionic Diffusion Through Cement Pastes

For the ease of presentation it is necessary to recapitulate some of the empirical observations. Most of the diffusion work on cement paste has been carried out using diffusion cells in which thin hardened paste barriers are inserted between moderately concentrated and very dilute solutions of the diffusants.

Most authors have analyzed their diffusion data in terms of the unmodified Fick's first law, i.e., as D_as. At this stage it will be useful if only the alkali halide diffusants are considered.

Most authors have found that alkali ions have lower D_as than the halide ions [12]. The situation is best illustrated by Figure 1 [13]. An analysis of Figure 1 throws much interesting light on various aspects of ion diffusion.

(a) Figure 1 shows that the diffusivity increases rapidly with the w/c ratio; however, the increase is steeper for Cs^+ ion than for I^- ion.

(b) Higher D_as of halide ions mean that more halide ions move to the low concentration side than alkali ions, i.e., some alkali ions are left behind. Obviously other ions are also moving at the same time to keep the electric charges balanced in the solutions on either side of the barrier. This means that Ca^{2+} ions move to the downstream side and OH^- ions move to the upstream side [14]. It appears that Ca^{2+} and OH^- ions can move in opposite directions without any imposed concentration gradients. It is obvious that the cement matrix strongly influences the process of ion diffusion through it.

(c) Increasing difference in the D_as between alkali and halide ions with decreasing w/c ratio indicates an increasing Ca^{2+} ion diffusion with decreasing w/c ratio. With the lowering w/c ratio the average pore size becomes increasingly narrow and the surface/volume ratio of the diffusion channels increases. Increasing surface/volume ratio of pores and increasing Ca^{2+} diffusion with lowering w/c indicates that Ca^{2+} concentration in the solution at the pore surface is high as against bulk pore solution. One may also infer that the cations are diffused mainly along the pore surfaces and the anions through the bulk pore solution, although some cations are also diffused through the bulk pore solution.

The high Ca^{2+} concentration at the pore surfaces could be identified with the high calcium concentration in the double layer solution. A detailed analysis of reference 13 suggests a selectivity factor of about 10 for Ca^{2+} ion over Na^+ ion in the double layer solution so that Ca^{2+} concentration is high in the double layer. This is in contrast to a very low concentration (about 1–3 millimole per liter) in the expressed pore solution [15]. It is of interest to note that a Ca^{2+} ion concentration of 8 millimole per liter has been measured in the downstream side during a diffusion experiment. This is much higher than that in the expressed pore solution. It is to be noted that to counterbalance the surface charges on the cement hydration products only half the number of Ca^{2+} ions are needed compared to the number of Na^+ ions.

All the above ion diffusion characteristics may be explained in the following manner.

(i) On a superficial level, the higher diffusivity of halide ions than that of alkali ions could be explained by noting that Ca^{2+} ion is also diffusing along with Na^+ and Cl^- to the downstream side. To maintain the electroneutrality on the downstream side, corresponding amounts of anions and cations must diffuse through the barrier. Since both Ca^{2+} and Na^+ ions are diffusing together, a smaller amount of Na^+ ion is transported to the downstream side than would be otherwise, i.e., the calculated diffusivity of Na^+ is lower than that of Cl^- ion. This, of course, raises the question as to why Ca^{2+} ion was diffusing to the downstream side.

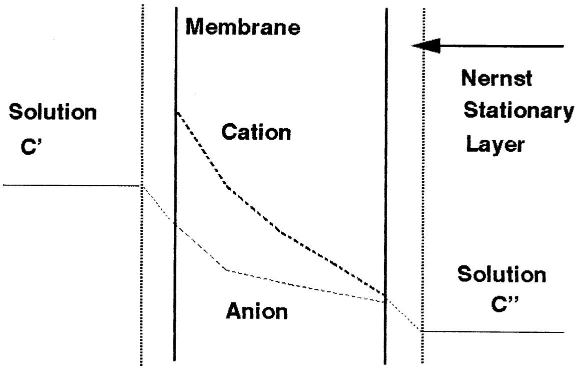

FIGURE 2. Anion and cation concentration profile in a Portland cement paste membrane.

However, a more satisfying explanation is the following. Consider a diffusion cell type experiment in which a thin cement paste barrier is interposed between a concentrated (e.g., 1 N) and a very dilute (e.g., 0.001 N) NaCl solution. The bulk pore solution is essentially an alkali hydroxide solution. The cement hydration products are negatively charged and the diffused double layer will have an excess of cations; in this case mainly Ca^{2+} with some Na^+. Soon after the start of the experiment, sodium and chloride ion concentrations in the bulk pore solution, within the paste barrier, at the upstream side approach 1 N NaCl concentration and at the downstream side 0.001 N NaCl [10,16]. The concentration gradient across the bulk pore solution will be about 1 N. In the absence of any other ion in the bulk pore solution only Na^+ and Cl^- will be diffused.

However, in the diffuse double layer the concentrations of cations at the upstream side will be much higher than 1 N; furthermore, Ca^{2+} will predominate. At the downstream side the concentration of the double layer solution will not be very different from that of the bulk pore solution. This means that the concentration gradient across the diffuse double layer will be much higher than that across the bulk pore solution. Figure 2 schematically shows the expected ion profiles in the double layer and bulk solutions in a Portland cement paste membrane. The diffusivity of the cations will, however, be governed by eq 7. The curvatures of the ion profiles shown in Figure 2 follow directly from eq 7.

The double layer concentration is mainly due to cations, so any diffusion through it will also be mainly that of cations. As the concentration of Ca^{2+} is very high in the double layer solution it will also be diffused to the downstream side even though there was no imposed concentration gradient for Ca^{2+}. Furthermore, as the difference in concentrations of Na^+ between the upstream diffusant solution and the double layer solution is comparatively low, not much Na^+ will diffuse to the downstream side, i.e., Na^+ will show a low phenomenologic diffusivity. The high concentration of Ca^{2+} in the double layer solution will be maintained by a continued dissolution of $Ca(OH)_2$ from the paste; OH^- ions move to the upstream diffusant solution to counterbalance its excess Na^+ ions. The overall charge balance among different transporting ions is maintained.

This implies that two ion diffusion processes occur simultaneously in the paste barrier: one through the double layer and the other through the bulk pore solution. Both the diffusion processes follow eq 7. The relative importance of the two processes varies with the size of the diffusion channels, i.e., with w/c ratio of the cement paste. With lowering of the w/c ratio the ion diffusion through the double layer will predominate; as a result Ca^{2+} migration to the downstream side solution will increase. Thus, the observation (a) and parts of (b) and (c) are explained.

(ii) The concentrations of Ca^{2+} and Na^+ ions are much higher in the double layer than of Cl^- in the bulk solution (see Table 1). Equation 7 suggests that the intrinsic diffusivities of Ca^{2+} and Na^+ ions are lower in the double layer than the intrinsic diffusivity of Cl^- in the bulk solution. However, the electroneutrality principle demands that corresponding amounts of negative and positive ions should diffuse. This brings Nernst-Planck interaction into operation and thereby the diffusivity of Cl^- is reduced and those of Ca^{2+} and Na^+ are increased. This explains the matrix effect of cement pastes. In the absence or near absence of the surface charge no such matrix effect is apparent, i.e., diffusion through a rock matrix. In the latter case Na^+ and Cl^- ions have the same diffusivity [17].

(iii) The maintenance of high Ca^{2+} ion concentration in the double layer solution by dissolving $Ca(OH)_2$ of Portland cement paste explains the comparatively high Cl^- diffusivity in this paste compared to pastes containing no $Ca(OH)_2$, e.g., slag-Portland cement paste [18]. Ca^{2+} ion, being doubly charged, replaces two Na^+ ions in the double layer so that the molar concentration of Ca^{2+} is half that of Na^+ ion at the same time the concentration of Na^+ ion is also reduced. This decrease in the molar concentration, compared to the case where there is only Na^+ ion is in the double layer, increases the diffusivity of ions in the double layer solution and thereby lowers the Nernst-Planck interaction, which in its turn increases the diffusivity of Cl^- ion in Portland cement paste. A similar phenomenon has been observed by Crooks and Quigley [19] in the case of saline leachate diffusion through a clay liner under a landfill. These authors studied a landfill site over 12 years. The original clay contained $CaCO_3$ and $MgCO_3$. Over the time Ca^{2+} and Mg^{2+} ions were leached out from the top of the clay liner and deposited at lower levels. At the top layer the diffusivity of Cl^- and Na^+ were 1×10^{-10} m^2/s each. At the lower layer Cl^- ion had a diffusivity of 6×10^{-10} m^2/s and that of Na^+ was 3.5×10^{-10} m^2/s. Notice that the diffusivities of both Cl^- and Na^+ ions are increased at the lower level; however, the increase was higher for Cl^- ion by a factor of 6. This differential increase in diffusivity could not be explained by any changes in porosity, tortuosity, geometry, etc. It means that the diffusivities of both Cl^- and Na^+ ions can be altered by changing the ion mix in the double layer solution, especially by introducing divalent ions. In the absence of Ca^{2+}, or Mg^{2+} ions in the double layer solution, i.e., in the absence of $CaCO_3$ or $MgCO_3$ in the upper clay layer, both Cl^- and Na^+ ions should have the same and low diffusivity mainly due to a very high concentration of Na^+ in the double layer solution and consequent lowering of its intrinsic diffusivity. Diffusion of alkali halide through slag-Portland cement paste has a striking similarity with that through top clay layer. A slag-Portland cement paste has no free $Ca(OH)_2$ and the diffusivity of alkali and halide ions are the same and lower than those through Portland cement paste [18]. The equal diffusivity of both alkali and halide ions through slag-Portland cement paste, as compared to their different diffusivity in Portland cement paste, could not be accounted for by any change in porosity, tortuosity, etc., of slag-Portland cement paste. The above noted alterations in the diffusivity of ions could not be predicted from the expressed solution chemistry.

The Formation Factor

In recent years a factor, *F*, variously known as "the formation factor" or "the lithologic factor" has been introduced in the cement literature. It is claimed that this factor incorporates all the interesting features of the pore system of a paste. This is defined as:

$$F = D_p/D_s \tag{9}$$

where D_p and D_s are the diffusivities of the pore solution and the paste sample [20]. The diffusivity measurement on expressed pore solution removes the matrix effect altogether. From the above discussions it appears that the meaning of the formation factor at moderate to low w/c pastes is very unclear; this is particularly so in the pastes where zeta-potential is high, e.g., in pastes containing unreacted silica fume. From Figure 1 it can be seen that the value of *F* depends on the choice of ion in the calculation; a cation and anion will not give the same value for the same D_p.

From Figure 1 it can be seen that the diffusivity of I^- ion increases by about three orders of magnitude over the w/c ratio between 0.2 to 0.7; for Cs^+ ion it is still higher. Within the same w/c range the water permeability increases by only two orders of magnitude [21]. This discrepancy also implies that the factor *F* does not incorporate all the features of the pore structure of a cement paste.

Pozzolanic Reaction, $Ca(OH)_2$ Crystal Growth, and Formation of Monosulfate

All the above processes require the movement of OH^-, Ca^{2+} ions, and water molecules. Both OH^- ion and water molecules are present throughout the aqueous phase. The concentration of Ca^{2+} ion is very low in a bulk (expressed) solution. If Ca^{2+} ions necessary for all the above processes have to be transported through the expressed solution, then they will be extremely slow. However, these processes are fairly rapid in saturated cement pastes. A high concentration of Ca^{2+} ion in the double layer solution provides an easy path for its diffusion.

Alkali-Silica Reaction and Deterioration due to the Presence of Dead-Burnt CaO and MgO

These aspects have already been discussed [1,22]. The main points are the following. In these cases, a high concentration of Ca^{2+} and/or Mg^{2+} ion in the double layer solution plays a very important role. In the case of alkali-silica reaction in Portland cement mortar or concrete it allows for the formation of Ca-rich layers on the reactive grains and the generation of expansive pressure. In the case of dead-burnt CaO or MgO it hampers dissolution and dispersion of $Ca(OH)_2$ or $Mg(OH)_2$ from CaO or MgO.

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