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On the relevance of electrochemical diffusion for the modeling of degradation of cementitious materials

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ABSTRACT

Reactive solute transport models have been broadly used over the last years to evaluate the durability of cementitious materials because they provide a mechanistic approach to cope with the complex diffusion–reaction phenomena involved in cement and concrete degradation processes. However, most of the numerical models published in the scientific literature use Fick's law as the constitutive equation for the diffusive transport of dissolved ions, neglecting the electrochemical constraints imposed by the various ionic fluxes, which conspire against the local electroneutrality of the system.

In this work, the relevance of electrochemical diffusion and its impact on the nonlinear coupled phenomena concerned by cement degradation were evaluated, on the basis of its influence on the simulation of deterioration of concrete exposed to weak sulfate solutions.

Results obtained show that diffusive approaches based on Fick's law may not be accurate enough for modeling the degradation of cementitious materials since, for the case considered, when ignored, electrochemical interactions in the diffusion process may lead to the inability of reactive transport models to reproduce key phenomena such as gypsum precipitation near the exposed cement surface.

1. Introduction

Over the last years, the study of concrete degradation has increasingly gathered the interest of the scientific community, in a certain measure due to the more stringent requirements of durability which are associated with the development of new materials (e.g., low-pH cements, sulfate-resisting cements, etc.) and relevant civil structures, such as nuclear waste repositories. In that context, the use of reactive transport models, capable of simulating the behavior of concrete under diverse boundary conditions has transcended the role of a mere complement of experimental studies and has become of paramount relevance in itself. Proof of this can be found in [1]. Through the use in very disparate hydrogeochemical systems, reactive transport models have gained in reliability over the years. Yet, cement being a very idiosyncratic material, there are things that are not quite settled. The debate that has been opened on the subject matter of the simulation of the transport of ionic species is evidence of the dynamic development of reactive transport modeling in this field of research.

Gradually, modelers have arrived to the realization that the problem cannot be formulated entirely in terms of molecular diffusion, for then the influence of forces arising from the generation of an electrical potential due to the movement of charged particles is neglected. As a consequence of the building up of an electrical potential, ions tend to move at different speeds from what could be expected on account of concentration gradients taken in isolation. Such divergences might or might not be of importance and thus the problem acquires shades of a practical nature, which can be reduced essentially to the following terms: Are actual results so different to justify the use of more demanding, complex, models? Is it worth the effort they entail when, as pointed out in [2], even the most sophisticated macroscopic models are unable to reproduce a number of non-standard phenomena when cement-based materials are dealt with? This dilemma has already been reckoned with [3], yet a conclusive answer remains to be given, and that is probably one of the main reasons that have prevented the Poisson–Nernst–Planck equations from achieving more widespread use, in comparison to the mathematically simpler, more straightforward, Fick's law. Thanks to the work of several researchers [3–11], however, a trend may be envisaged towards the reversal of the current state of affairs.

The objective of this paper is to contribute to this discussion by analyzing a problem which was already published in the scientific literature, although focused from an altogether different standpoint. Indeed, the paper which is being referred to [4], which deals with the effect of weak sulfate solutions on the durability of concrete, was originally oriented towards the verification of a reactive

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transport model developed by the authors, by means of the numerical simulation of the degradation of concrete under such aggressive conditions. On the other hand, the same example will be used herein to analyze the divergence of two different conceptual models of diffusive transport of electrically charged particles in aqueous solutions, with special attention to the coupled dissolution/precipitation processes evolving in the solid matrix.

2. Description of the two models for diffusion of ionic species

2.1. Fick's law

The contact of two different kinds of water is crucial for the process of degradation to unfold as it alters the reigning equilibrium of the concrete pore solution and gives rise to the transport of aqueous species at expense of the gradient of concentration between them. The application of the mass conservation equation for a given ionic species diffusing in the liquid phase yields:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (j_i) = 0 \tag{1}$$

where c_i is the concentration of the considered species in solution and j_i is the flux of the same species in the liquid phase. If the flux is taken to be proportional to the gradient of concentration of the species considered, as:

$$j_i = -D_i \nabla c_i \tag{2}$$

where D_i is the diffusion coefficient of the species, then Eq. (1) turns into the well-known Fick's second law

$$\frac{\partial c_i}{\partial t} = \nabla \cdot (D_i \nabla c_i) \tag{3}$$

As is well known, Fick's law applies when dealing with molecular diffusion, providing the exact solution of the problem. The conceptual model that Fick's law entails is, however, not entirely reliable when the movement of ionic species is involved, for it neglects the particular features of ionic diffusion mechanisms in liquids. Indeed, unlike neutral molecules, ions are electrically charged particles and they are subjected to various electrical forces. The charged nature of the ionic particles is at the origin of various interactions between the drifting particles (ion/ion and ion/solvent interactions). These so-called activity effects become important as the concentration of the various ions in solution increase. The electrical charge of the particles may also contribute to generate specific ion/solid interactions.

2.2. The Poisson–Nernst–Planck equations

Despite the relative importance of activity effects and ion/solid interaction phenomena, the most relevant feature which distinguishes ion diffusion from molecular diffusion involves the electrical coupling of the various ionic fluxes. Indeed, during the diffusion process, the different ionic species tend to drift at divergent speeds (in response to their respective concentration gradients and diffusion coefficients in the medium where the movement takes place) thus inducing electrical unbalances which conspire against the local electroneutrality of the system. Nevertheless, any local excess charge transferred by the ions movement generates an electrical field (referred to as diffusion potential) which tends to restore the electroneutrality by harmonically altering the diffusion rate of all the species involved.

Diffusion transport of ionic species is therefore constrained by the electroneutrality requirement, which should hold at any point of the liquid phase. Electroneutrality is evaluated by lumping the electric contribution of all the species present in solution. This requirement is taken into account by the Poisson–Nernst–Planck equations, according to which j_i can be defined as follows [7]:

$$j_i = -D_i^{\mu}\,\mathrm{grad}(c_i) - \frac{D_i^{\mu} z_i F}{RT} c_i\,\mathrm{grad}(\psi) - D_i^{\mu} c_i\,\mathrm{grad}(\ln \gamma_i) \tag{4}$$

where R is the ideal gas constant; F is the Faraday constant; T is the absolute temperature; z_i is the valence of the ionic species; γ_i is the chemical activity coefficient of the chemical species; and D_i^{μ} is the diffusion coefficient in the liquid phase, assumed to be an ideal solution. Finally ψ stands for the diffusion potential set up by the drifting ions, according to the Poisson equation [12]:

$$\nabla^2 \psi - \frac{\rho}{\varepsilon} = 0 \tag{5}$$

where ε is the permittivity of the medium and ρ represents the electrical charge density, which is defined as:

$$\rho = F \sum_{i=1}^{N} z_i c_i \tag{6}$$

N being the number of ionic species in solution.

The calculation of the chemical activity coefficient in Eq. (4), might be carried out by means of, for instance, the expression of Debye–Hückel (Eq. (7)), which was found to give accurate results [13]:

$$\ln \gamma_i = -\frac{A z_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + bI \tag{7}$$

where A and B and b are temperature-dependent parameters; a_i is a constant characteristic of a given species; and I is the ionic strength of the solution, defined as:

$$I = \frac{1}{2} \sum_{i=1}^{N} z_i^2 m_i \tag{8}$$

where m_i represents the molality of the i-th ionic species.

Thus, two different approaches were outlined, namely, those provided by Fick's and the Poisson–Nernst–Planck laws. One of the obvious advantages of Fick's law lies on its extremely simple mathematical formulation, which has favored its use in a wide range of practical problems. In fact, Fick's law provides accurate results for diffusive transport problems of neutral species. Its applicability could, nevertheless, be subjected to question when dealing with multi-solute diffusion problems, for the effects of electrical gradients might no longer be negligible. Both the Poisson–Nernst–Planck equations and Fick's law will be tested in the next section in relation to the water–concrete interaction problem which was previously set up.

3. Description of the experiment

The subject matter of the simulation is the case of a concrete slab resting on a sulfate contaminated soil. The scheme of the experiment under simulation is seen in Fig. 1. As can be seen, the thickness of the slab was fixed at 15 cm and the bottom part of it was considered to be directly in contact with the soil (containing Na^+ and SO_4^{2-} ions).

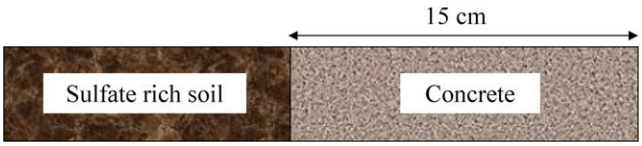

Fig. 1. Schematic representation of the modeled problem.

On the other hand, the interstitial solution contained in the porous structure of the cement paste is highly charged with alkaline Na^+, K^+, OH^- and Ca^{2+} ions.

It is worth pointing out here that, since the original intention of the cited research [4] was to evaluate the performance of different kinds of concrete – in particular, that of sulfate-resisting cement in relation to ordinary Portland cement – several scenarios were set up, under both saturated and unsaturated conditions, involving a wide range of water-to-cement ratios and of the concentration of sodium sulfate in the aggressive solution.

The scope of the present work is, nonetheless, narrower, as it is focused only on a single case, where the saturated hardened paste is made of CSA type 50 cement, with a water-to-cement ratio of 0.65, and the concentration of sodium sulfate in the boundary water is fixed at 10 mmol/L. The initial composition of the pore solution, the mineralogical distribution of the unaltered cement paste and the porosity of the mixture for that particular concrete are given in Table 1. For more details, the reader is referred to [4].

Calcite, gypsum, quartz and amorphous silicon, although initially absent, were also taken into account in case precipitation could take place. As shown in Table 1, the influence of coarse and fine aggregates was also considered by means of a fictitious mineral, capable of dissolving into calcium and bicarbonate ions, and which occupies 71.90% of the total volume.

As reported in [4], the computer code STADIUM, which takes into consideration the coupled transport of ions and liquid and the chemical equilibrium of solid phases within the saturated system, was used in order to investigate the process of concrete degradation. The numerical model has proven reliable at simulating the deterioration of hydrated cement systems subjected to sulfate attack and calcium leaching [6,10]. The numerical modeling tool applied herein, CrunchFlow [14], is a computer program for multicomponent reactive transport in porous media. CrunchFlow is an enhanced version of the GIMRT/OS3D package [15,16] which can be used for reactive transport problems of arbitrary complexity and size (i.e., there is no a priori restriction on the number of species or reactions considered). Some of its main features include the simulation of advective, dispersive, and diffusive transport in up to two dimension using the global implicit (GIMRT) option; non-isothermal transport and reaction; multicomponent aqueous complexation; kinetically-controlled mineral precipitation and dissolution; and reaction-induced porosity and permeability feedback to both diffusion and flow.

In the following, advantage will be taken of the capability of CrunchFlow of simulating transport by either molecular or ionic diffusion, i.e., by either Fick's law or the Poisson–Nernst–Planck equations, respectively. As said above, the application of the latter requires the determination of the specific diffusion coefficient of each ionic species. These were provided by means of migration tests carried out by Samson et al. [17] on cylindrical samples of 25 mm thickness.

Table 1
Physicochemical characteristics of the hardened cement paste.

Aqueous species		Concentration (mmol/L)
Initial pore solution		
OH^-		183.42
Na^+		71.40
K^+		108.90
SO_4^{2-}		1.17
Ca^{2+}		2.74
$Al(OH)_4^-$		0.03
Mineral phase	Weight (g/kg)	Volume fraction (%)
Initial solid phase		
Portlandite	38.10	4.00
C–S–H	76.10	8.77
Ettringite	12.40	1.33
Hydrogarnet	4.30	0.40
Aggregates		71.90
Porosity		13.60

Results are reproduced from [4] and shown in Table 2.

A total of 31 homogeneous hydrogeochemical reactions and 8 precipitation/dissolution mineral processes were considered in the modeling and are listed in Table 3.

A numerical simulation was carried out over a period of 20 years, in order to test the performance of CrunchFlow in contrast to that of STADIUM.

Numerical simulations were then carried out over a period of 2500 days. The conditions of the problem were in all cases designed to properly reproduce those of the original model, in relation to the chemical composition of both the interstitial solution and the boundary water as well as the mineralogical composition of concrete. The thickness of the slab was discretized into 150 constant-size elements of 0.1 cm each.

4. Results of the numerical simulations

4.1. Verification of the numerical model

Before proceeding to set forth in further detail the subject matter of this work, it is worth corroborating whether or not the results obtained with CrunchFlow match those reported in [4] whenever they are indeed comparable. The problem was solved using the Poisson–Nernst–Planck formulation for the description of ionic transport which was, as said above, also the choice made in [4].

Fig. 2 shows the results obtained in [4] and in the present work. Whereas the overall picture exhibits an analogous pattern for the distribution of the mineral phases, divergences are instantly apparent from the extent of the penetration reached by the degradation fronts. These discrepancies might be attributed to the fact that the effective diffusion coefficients, as calculated by either STADIUM or CrunchFlow, obey two different constitutive relationships. In fact, the numerical model STADIUM follows [18]:

$$\frac{D_{\text{eff}}}{D_0} = [0.001 + 0.07\phi^2 + 1.8H(\phi - \phi_c)(\phi - \phi_c)^2] \tag{9}$$

where D_{eff} and D_0 denote the effective diffusion coefficients and diffusion coefficients in water, respectively; ϕ represents the capillary porosity of concrete and $\phi_c = 0.18$ is a critical constant dependent on the material; and $H(\phi - \phi_c)$ is the Heavyside function.

On the other hand, CrunchFlow assumes that the variation of the effective diffusion coefficients in the porous medium as a function of the capillary porosity is reasonably well approached by [5]:

$$D_{\text{eff}} = \frac{D_0}{\phi^m F} \tag{10}$$

where the parameters $F = 140.533$ and $m = 1.0$ are respectively the formation factor and the cementation exponent.

Table 2
Specific effective diffusion coefficients, as reported by Marchand et al. [4].

Species	Effective diffusion coefficient (m^2/s)
OH^-	25.8E−11
Na^+	6.50E−11
K^+	9.60E−11
SO_4^{2-}	5.20E−11
Ca^{2+}	3.90E−11
SO_4^{2-}	2.70E−11

Table 3
Hydrogeochemical reactions considered in the reactive transport model.

Homogeneous hydrogeochemical reactions	log *K*
$H^+ + OH^- \leftrightarrow H_2O$	+13.9951
$Al^{3+} + 2H_2O \leftrightarrow AlO_2^- + 4H^+$	−22.8833
$Al(OH)_2^+ + 2H^+ \leftrightarrow Al^{3+} + 2H_2O$	+10.5945
$AlOH^{2+} + H^+ \leftrightarrow Al^{3+} + H_2O$	+4.9571
$Al(SO_4)_2^- \leftrightarrow Al^{3+} + 2SO_4^{2-}$	−4.9000
$AlSO_4^+ \leftrightarrow Al^{3+} + SO_4^{2-}$	−3.0100
$CaCO_{3(aq)} + H^+ \leftrightarrow Ca^{2+} + HCO_3^-$	+7.0017
$CaCl^+ \leftrightarrow Ca^{2+} + Cl^-$	+0.6956
$CaCl_{2(aq)} \leftrightarrow Ca^{2+} + 2Cl^-$	+0.6436
$CaHCO_3^+ \leftrightarrow Ca^{2+} + HCO_3^-$	−1.0467
$CaOH^+ + H+ \leftrightarrow Ca^{2+} + H_2O$	+12.8500
$CaSO_{4(aq)} \leftrightarrow Ca^{2+} + SO_4^{2-}$	−2.1111
$CO_{2(aq)} + H_2O \leftrightarrow H^+ + HCO_3^-$	−6.3447
$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$	+10.3288
$HAlO_{2(aq)} + 3H^+ \leftrightarrow Al^{3+} + 2H_2O$	+16.4329
$HCl_(aq) \leftrightarrow Cl^- + H^+$	−0.6700
$H_2SiO_4^{2-} + 2H^+ \leftrightarrow SiO_{2(aq)} + 2H_2O$	+22.9600
$HSiO_3^- + H^+ \leftrightarrow SiO_{2(aq)} + H_2O$	+9.9525
$H_2SO_{4(aq)} \leftrightarrow SO_4^{2-} + 2H^+$	+1.0209
$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$	−1.9791
$KCl_{(aq)} \leftrightarrow Cl^- + K^+$	+1.4946
$KHSO_{4(aq)} + H^+ \leftrightarrow H^+ + K^+ + SO_4^{2-} +$	−0.8136
$KOH_{(aq)} + H^+ \leftrightarrow H_2O + K^+$	+14.4600
$KSO_4^- \leftrightarrow K^+ + SO_4^{2-}$	−0.8796
$NaAlO_{2(aq)} + 4H^+ \leftrightarrow Al^{3+} + Na^+ + 2H_2O$	+23.6266
$NaCl_{(aq)} \leftrightarrow Cl^- + Na^+$	+0.7770
$NaHCO_{3(aq)} \leftrightarrow HCO_3^- + Na^+$	−0.1541
$NaHSiO_{3(aq)} + H^+ \leftrightarrow H_2O + Na^+ + SiO_{2(aq)}$	+8.3040
$NaCO_3^- + H^+ \leftrightarrow HCO_3^- + Na^+$	+9.8144
$NaOH_{(aq)} + H^+ \leftrightarrow H_2O + Na^+$	+14.7948
$NaSO_4^- \leftrightarrow Na^+ + SO_4^{2-}$	−0.8200

Mineral processes	log *K*	Molar volume (cm^3/mole)
Portlandite $\leftrightarrow Ca^{2+} + 2OH^-$	−5.2000	33.056
C—S—H $\leftrightarrow Ca^{2+} + 2OH^-$	−5.6000	95.100
Gypsum $\leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	−4.6000	74.690
Ettringite $\leftrightarrow 4OH^- + 2AlO_2^- + 3SO_4^{2-} + 6Ca^{2+}$	−44.0000	569.890
Hydrogarnet $\leftrightarrow 4OH^- + 2AlO_2^- + 6Ca^{2+}$	−23.0000	149.520
Quartz $\leftrightarrow SiO_{2(aq)}$	−3.9993	22.688
$SiO_{2(s)} \leftrightarrow SiO_{2(aq)}$	−2.7136	29.000
Calcite $+ H^+ \leftrightarrow Ca^{2+} + HCO_3^-$	+1.8487	36.934

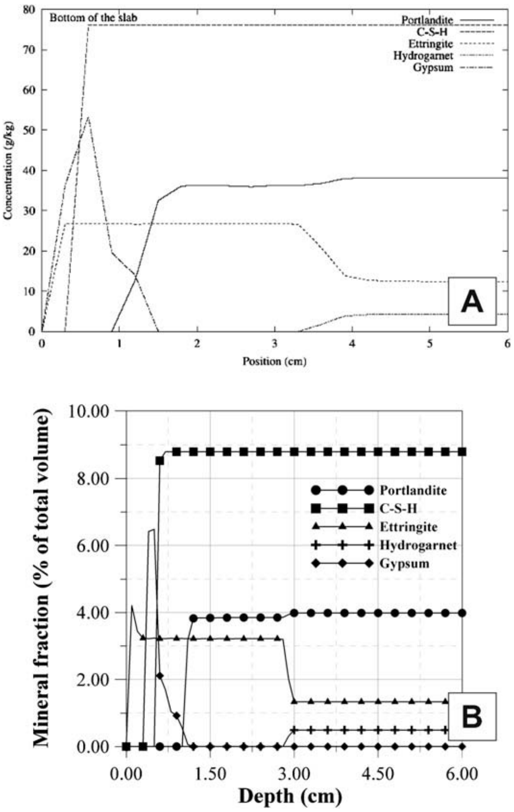

Fig. 2. Distribution of the solid phases after 20 years for the concrete under analysis. A. Results reported in Marchand et al. [4] and B. Results obtained in the present work.

Another source of disagreement lies in the formulation of the activity coefficients chosen in [4] which, in contrast to the Debye–Hückel equation used in this work, consists of a modification of the Davies equation

$$\ln \gamma_i = -\frac{Az_i^2\sqrt{I}}{1 + a_iB\sqrt{I}} + \frac{(0.2 - 4.17E - 05I)Az_i^2 I}{\sqrt{1000}} \tag{11}$$

The mentioned differences notwithstanding, in view of the output of CrunchFlow as shown in Fig. 2, it can be assumed that the phenomenology of the process is reliably reproduced. This will emerge even more patently in the following, as further evidence will be provided.

4.2. Results assuming diffusion transport is ruled by the Poisson–Nernst–Planck equations

The evolution of the concentration of aqueous species in the pore solution, as simulated by CrunchFlow, is shown in Fig. 3. It is clearly seen that one of the earliest effects of degradation is the depletion of alkali ions, which is followed by an increase in calcium concentration, at the expense of the dissolution of portlandite and the decalcification of C–S–H. The concentration of calcium after 2500 days displays a gently sloped profile behind the first front, as calcium ions are released to provide a source for ettringite to precipitate. A peak is reached of about 26 mmol/L, and then an abrupt decline, which rules the leaching of calcium ions out of interstitial solution towards the boundary water. Sulfate ions reach also a relatively high concentration near the surface. It is remarkable that the highest peak is located some millimeters inside the concrete slab and not on its surface, where it would be expected to be had only molecular diffusion been considered, as the boundary water is the main source of sulfate ions. This particular feature is related to the influence of electrical forces on the movement of charged particles.

The statement made by Marchand et al. [4], as to that the 'internal reorganization' of the geochemical composition of the concrete slab is affected by the advance of degradation fronts that steadily penetrate from its external surface towards its center is clearly illustrated in Fig. 4, where the evolution of the solid phases during the prescribed time of simulation is shown. Alongside the formation of ettringite, which is the most well known and worrisome consequence of the sulfate attack, also the precipitation of gypsum near the exposed surface is predicted by the model. As noted in [4], these results are in good correlation with most investigations on this subject. Additional evidence can be found in [6].

The precipitation of ettringite is mostly explained by the presence of aluminum in excess in the pore solution, as a result of the dissolution of hydrogarnet. Yet, once all the hydrogarnet is dissolved, the source of aluminum vanishes, which impedes the further precipitation of ettringite. On the other hand, the dissolution

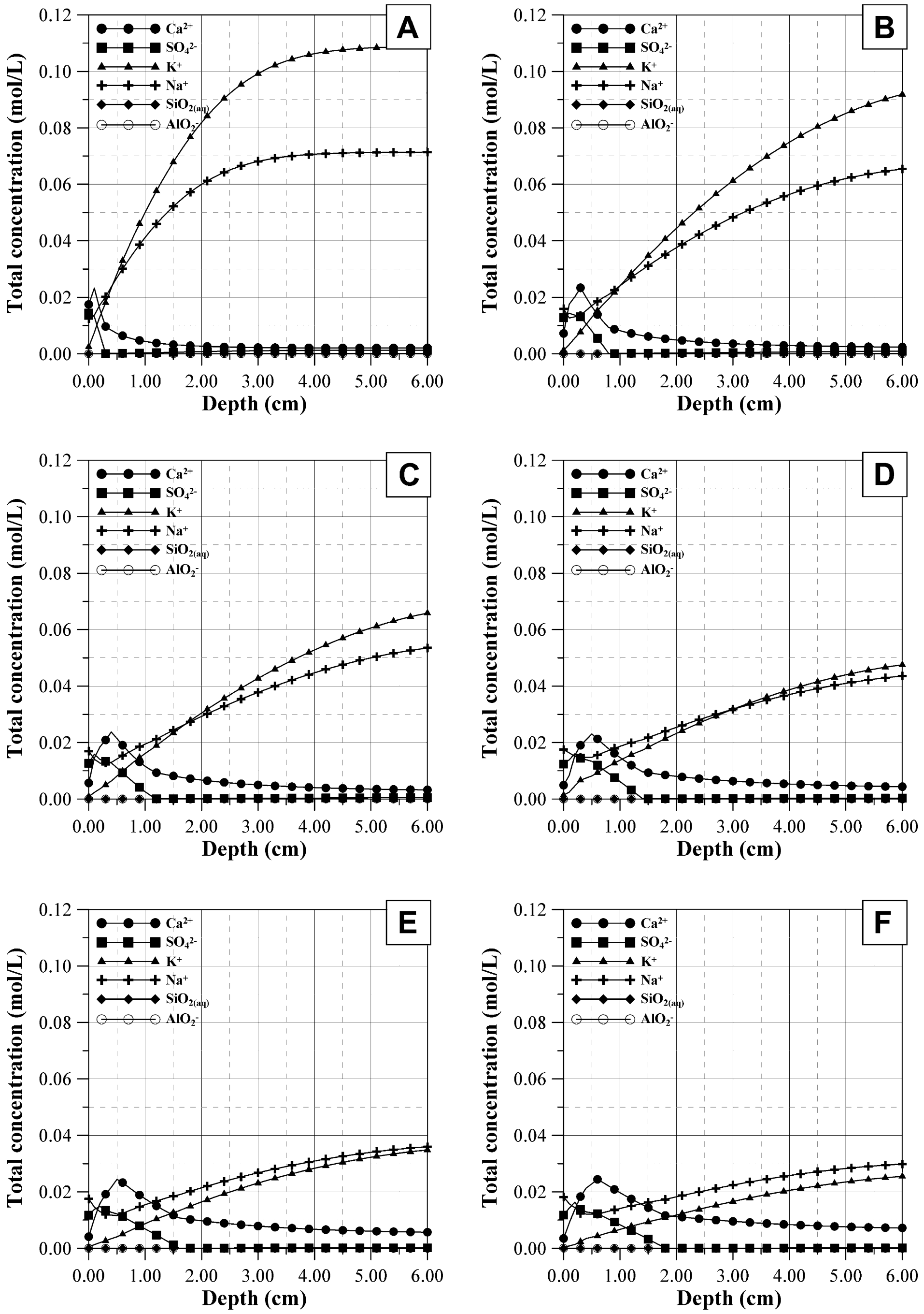

Fig. 3. Aqueous species concentration after 100 (A), 500 (B), 1000 (C), 1500 (D), 2000 (E) and 2500 days (F), assuming diffusion is ruled by the Poisson–Nernst–Planck equations.

of portlandite and decalcification of C–S–H, for which there is also experimental evidence, induces the rise of concentration of calcium. The rise of concentration of calcium in the interstitial solution, in conjunction with that of sulfate, causes the saturation index to turn critical.

4.3. Results assuming diffusion transport is ruled by Fick's law

A second series of simulations was performed with CrunchFlow, this time employing Fick's law to describe diffusion phenomena. Accordingly, all species were assumed to have the same diffusion coefficient. That unique diffusion coefficient was equal to the average of the specific diffusion coefficients assigned to each of them when using the Poisson–Nernst–Planck equations.

Fig. 5 shows the evolution of the chemical composition of the pore solution with depth at different times. Three divergent aspects are particularly noticeable with respect to the results obtained with the Poisson–Nernst–Planck equations. First, the sodium profile after 2500 days exhibits a much milder slope when the diffusion gradient reverses, thus preserving somewhat the alkaline conditions in the pore solution and buffering the leaching of calcium ions. Second, as a consequence, the peak of calcium concentration decreases down to approximately 1.85 mmol/L. Finally, unlike the previous case, the sulfate concentration profile displays

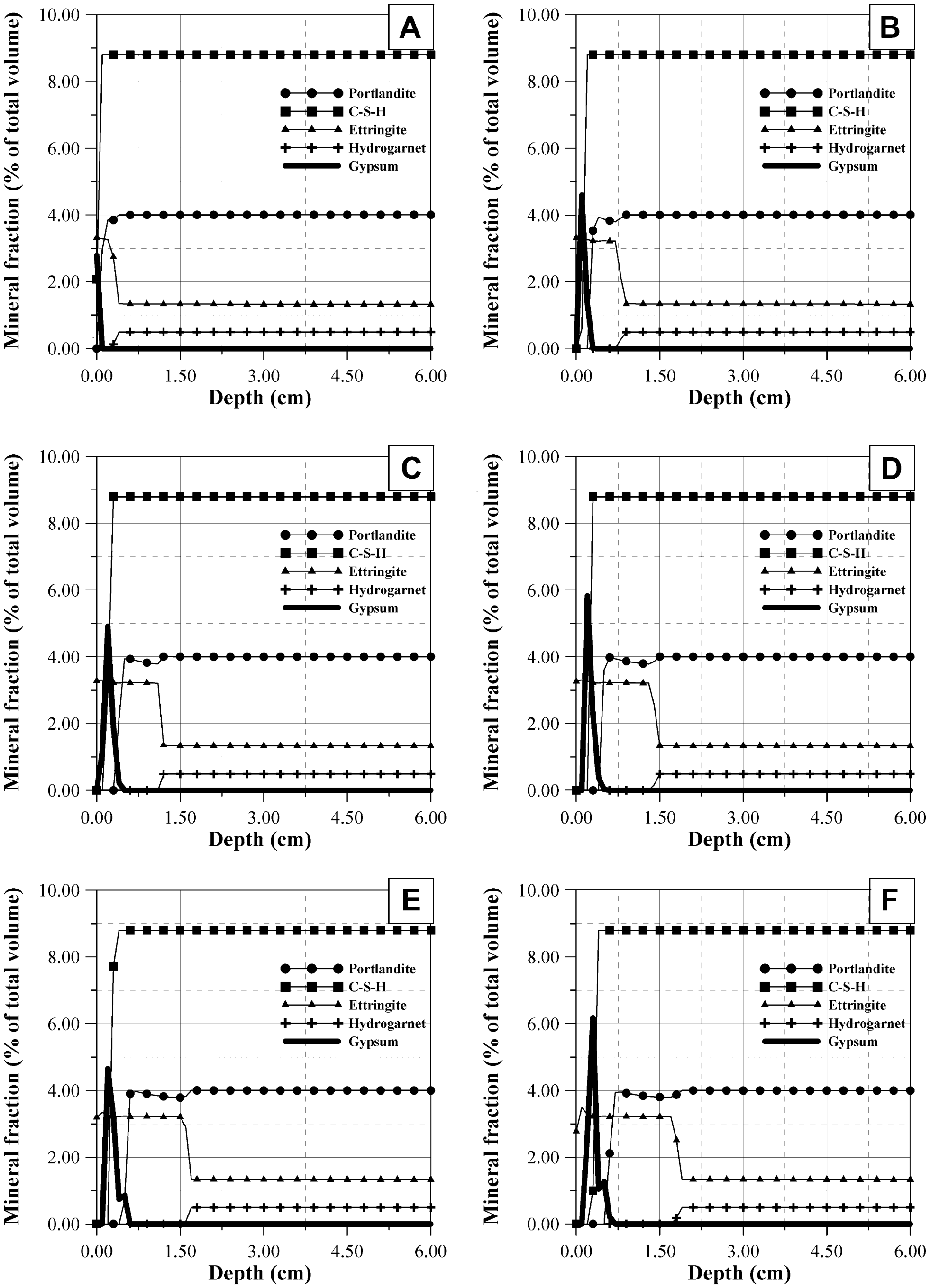

Fig. 4. Distribution of the solid phases after 100 (A), 500 (B), 1000 (C), 1500 (D), 2000 (E) and 2500 days (F), assuming diffusion is ruled by the Poisson–Nernst–Planck equations (gypsum precipitation was highlighted with a thick solid line).

a gradual decline from the exposed surface towards the center of the slab.

The mineral evolution of the solid phase is shown in Fig. 6.

As can be observed, results computed by assuming that ionic diffusion can be described by Fick's law (Fig. 6) show a similar pattern with respect to those obtained when using the Poisson–Nernst–Planck approach (Fig. 4). Mainly two fronts evolve from the surface towards the center of the slab – the first one denoted by the dissolution of hydrogarnet and precipitation of ettringite, and the second one by dissolution of portlandite and C–S–H. All mineral components develop roughly in an analogous manner to that predicted by the Poisson–Nernst–Planck equations, except for gypsum, which does not precipitate at all, since calcium and sulfate are present in smaller amounts in the interstitial solution, and the system is below the saturation threshold.

This point is more explicitly illustrated in Fig. 7. Given that the solubility constant of gypsum is, by definition:

$$K_{\text{gypsum}} = \left[\mathrm{Ca}^{2+}\right]\left[\mathrm{SO}_4^{2-}\right] = \left(\gamma_{\mathrm{Ca}^{2+}} m_{\mathrm{Ca}^{2+}}\right)\left(\gamma_{\mathrm{SO}_4^{2-}} m_{\mathrm{SO}_4^{2-}}\right) \tag{12}$$

where $[\mathrm{Ca}^{2+}]$ and $[\mathrm{SO}_4^{2-}]$, and $m_{\mathrm{Ca}^{2+}}$ and $m_{\mathrm{SO}_4^{2-}}$ are the activities and the molal concentration of calcium and sulfate, respectively.

Then, operating and rearranging, the following formula is obtained:

$$\log\left(\gamma_{\mathrm{SO}_4^{2-}} m_{\mathrm{SO}_4^{2-}}\right) = \log K_{\text{gypsum}} - \log\left(\gamma_{\mathrm{Ca}^{2+}} m_{\mathrm{Ca}^{2+}}\right) \tag{13}$$

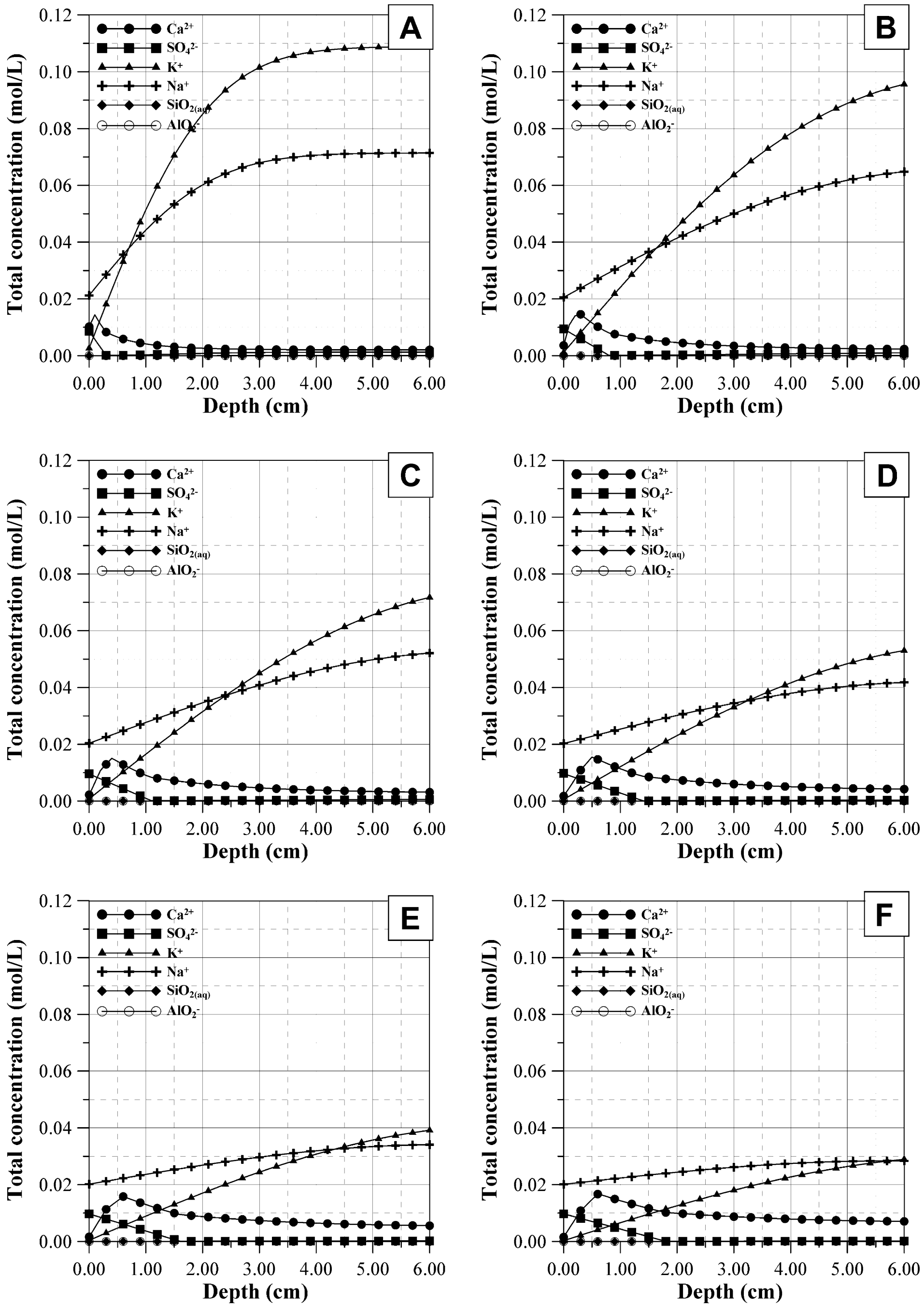

Fig. 5. Aqueous species concentration after 100 (A), 500 (B), 1000 (C), 1500 (D), 2000 (E) and 2500 days (F), assuming diffusion is ruled by Fick's law.

which is the equation of the solid line shown in Fig. 7. The space above that line denotes an oversaturation state with respect to gypsum. Dotted lines each represent the state of the pore solution over a depth of 6 cm (measured from the exposed surface of the slab) at a particular time step. As can be seen, given that Fick's law underestimates the peak concentration of both calcium and sulfate in the pore solution, all points sampled appear to remain slightly, but consistently, undersaturated with respect to gypsum.

Simulations made contemplating the Poisson–Nernst–Planck equations, on the other hand, result in a global shift towards saturation. At any time step considered, points exist that are lying on the equilibrium curve, which is in correspondence with the actual precipitation of gypsum shown in Fig. 4 and validated by experimental evidence [6].

5. Conclusions

A numerical simulation of the deterioration of concrete exposed to a weak sulfate solution was carried out and analyzed under the framework of two different formulations for the diffusive ionic transport in the aqueous phase, namely Fick's law and the Poisson–Nernst–Planck equations. It was found that, in spite of some minor divergences (presumably arising from both the different constitutive relationships porosity–diffusivity and the definition of the activity coefficients used in either the original paper or the present work), the results obtained in this work are coherent and entirely comparable with those reported previously, thus providing support and confidence on both independent models.

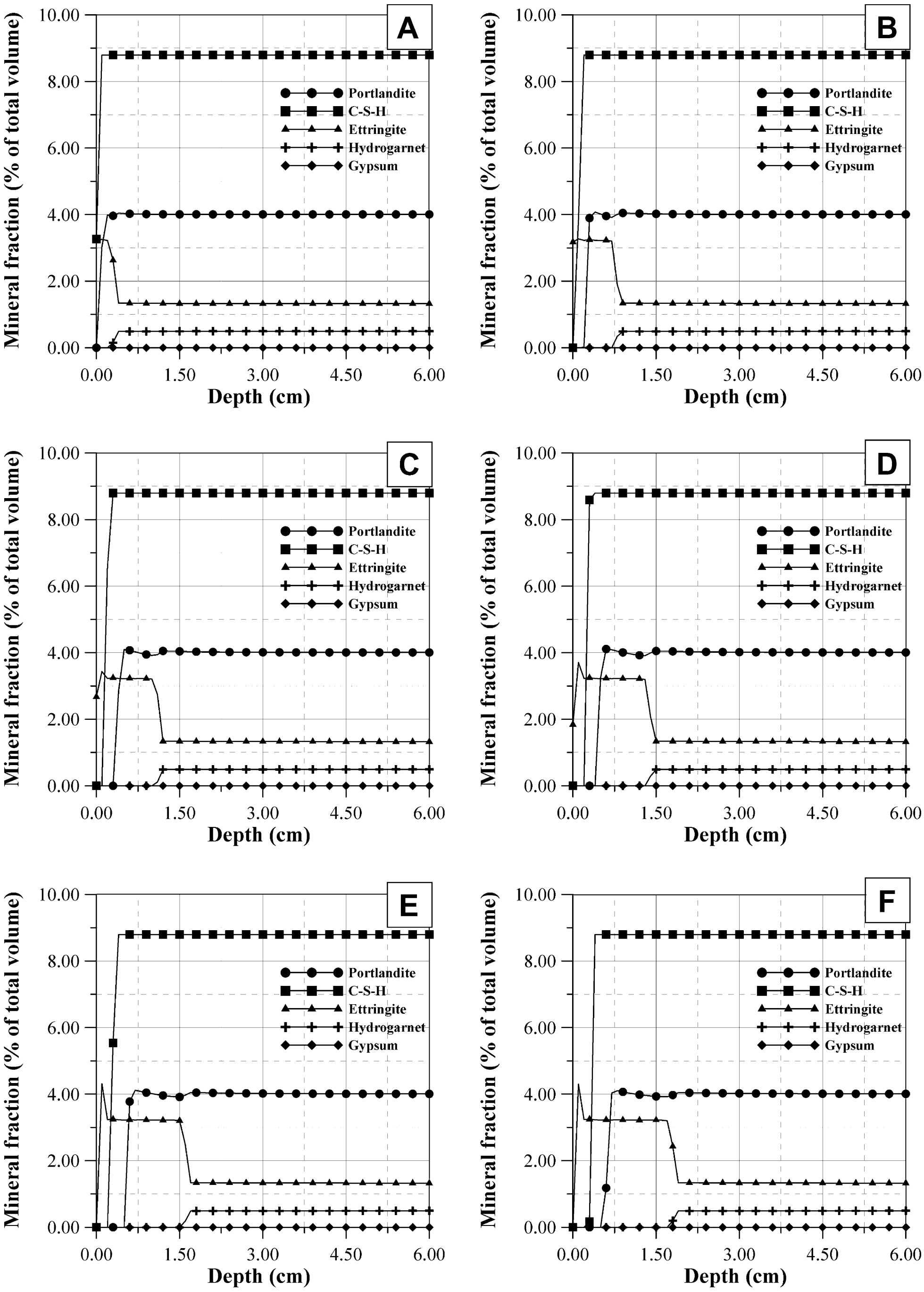

Fig. 6. Distribution of the solid phases after 100 (A), 500 (B), 1000 (C), 1500 (D), 2000 (E) and 2500 days (F), assuming diffusion is ruled by Fick's law.

The model set-up was used to compare the performance of the two theoretical conceptualizations of diffusion transport. On comparing the performance of Fick's law and the Poisson–Nernst–Planck equations, results show that the former fails to reproduce the precipitation of a thin layer of gypsum close to the exposed surface of concrete. The reasons behind this anomaly lie in the fact that Fick's law tends to underestimate the actual concentration of calcium and sulfate in the pore solution (which, on the other hand, is better predicted by the Poisson–Nernst–Planck equations), thus preventing it from reaching the saturation threshold with respect to gypsum.

Given that the precipitation of gypsum was corroborated by experimental studies, the preceding analysis raises the question as to which extent purely diffusive approaches are appropriate in modeling transport processes of electrically charged species in porous media in general and in cement-based materials in particular.

As was proved for the case analyzed, neglecting electrochemical interactions in the diffusion process may lead to the inability of the reactive transport models to reproduce such key phenomena as gypsum precipitation for sulfate attack scenarios, because of which it can be concluded that purely diffusive approaches based on Fick's law may not be accurate enough for modeling the degradation of cementitious materials. To that aim, in light of the results obtained, the Poisson–Nernst–Planck equations may provide a more suitable alternative framework.

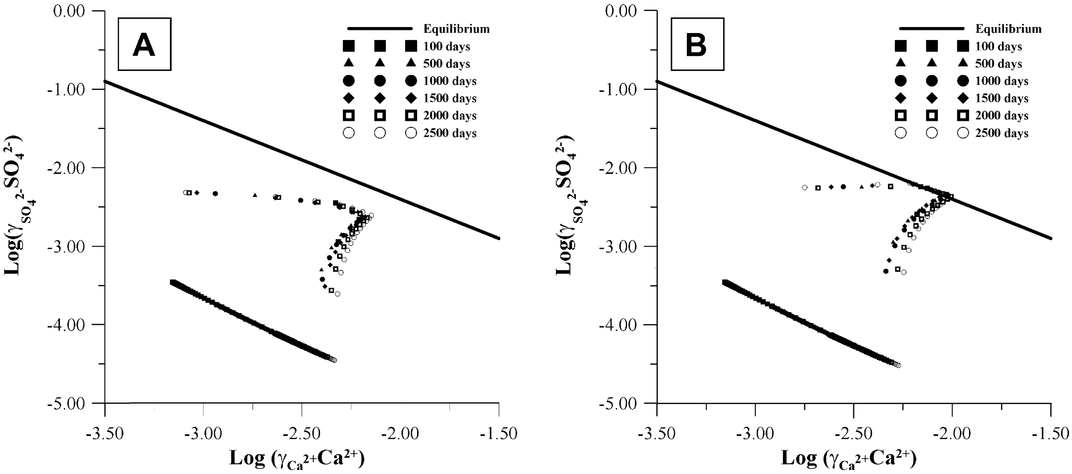

Fig. 7. Saturation state of the pore solution with respect to gypsum. (A) Simulation results obtained using Fick's law and (B) Simulation results obtained using the Poisson–Nernst–Planck equations.

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