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A MATHEMATICAL MODEL IN CHARACTERING CHLORIDE DIFFUSIVITY IN UNSATURATED CEMENTITIOUS MATERIALS

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SUMMARY: In this paper, a new analytic model for predicting chloride diffusivity in unsaturated cementitious materials is developed based on conductivity theory and Nernst-Einstein equation. The model specifies that chloride diffusivity in unsaturated cementitious materials can be mathematically described as a function of chloride diffusivity in saturated state, water saturation and average pore diameter of the material. A series of experiments were conducted in order to validate the model. Mortar samples with varying cementitious mixtures were cast and cured for one year, followed by oven drying at 50 °C until desired water saturation levels (18 to 100 %) and homogeneous moisture distribution were obtained. The electrical conductivities of mortar specimens at various water saturations were measured and then converted into chloride diffusivities by using Nernst-Einstein equation. It is found that the experimental results can be well described by the analytic model proposed in this work.

MATEMATIČKI MODEL PRIKAZA DIFUZIJE KLORIDA U NEZASIĆENIM CEMENTNIM MATERIJALIMA

SAŽETAK: U radu je prikazan novi analitički model predviđanja difuzije klorida u nezasićenim cementnim materijalima na osnovi teorije vodljivosti i Nernst-Einsteinove jednadžbe. Model prikazuje da se difuzija klorida u nezasićenim cementnim materijalima može matematički opisati kao funkcija difuzije klorida u zasićenom stanju, funkcija zasićenosti vodom i funkcija prosječnoga promjera pora u materijalu. Radi vrednovanja modela proveden je niz pokusa. Izrađeni su uzorci morta s različitim cementnim mješavinama i njegovani jednu godinu. Zatim su osušeni u sušioniku na 50 °C sve dok nisu postignute željene razine zasićenja vodom (od 18 % do 100 %) i homogena raspodjela vlage. Izmjerena je električna vodljivost uzoraka morta pri različitim zasićenjima vodom što je potom pretvoreno u difuziju klorida primjenom Nernst-Einsteinove jednadžbe. Utvrđeno je da se eksperimentalni rezultati mogu dobro opisati analitičkim modelom predloženim u ovom radu..

1. INTRODUCTION

The resistance to chloride diffusion is a major concern for the durability of reinforced concrete in cases of structures being exposed to seawater or deicing salts. Current durability design, e.g. DuraCrete, usually relies on measuring chloride diffusivity in saturated concrete. However, on-site concrete is seldom saturated due to long term self-desiccation or drying-wetting cycles. To effectively design new reinforced concrete structures, a reliable model for describing the relationship between saturated and non-saturated chloride diffusivity should be used.

In cementitious materials, the parameter relative chloride diffusivity (D_{rc}) is defined as the ratio between chloride diffusivity at a particular moisture condition and that at saturated condition. In the past decades, a few models have been reported for the determination of D_{rc} [1-3]. By fitting experimental results, Saetta et al. [1] proposed an S-shaped relationship that the D_{rc} was the first time expressed as a function of interior relative humidity. Buchwald [2] estimated the ionic diffusivity by impedance spectroscopy measurement and proposed a power equation which relates D_{rc} to the degree of water saturation (S_w). Zhang et al. [2012] simulated the ionic diffusivity in unsaturated cement pastes with w/c ratios of 0.4, 0.5 and 0.6 by using lattice Boltzmann method; a quadratic polynomial equation was used to describe the D_{rc} at various water saturation S_w levels.

It is noteworthy that these existing models for the determination of D_{rc} are all empirical-based. Up to date there is no consensus on the reliable description of D_{rc}. The aim of this paper is trying to, from scientific point of view, develop a new analytic model to describe the D_{rc}-S_w relation. To this end, the conductivity theory and Nernst-Einstein equation are applied and linked to microstructural parameters. A series of conductivity experiments are performed on mortar specimens at various S_w levels. The experimental results are used to validate the proposed analytic model.

2. MATHEMATICAL MODEL OF NON-SATURATED CHLORIDE DIFFUSIVITY

In porous media, diffusion of chloride ions is driven by the concentration gradient of chloride ions. Electrical conduction of chloride ions results from electrical potential differences. In principle, the two types of ionic movements are inherently correlated by Nernst-Einstein equation. In this study, a combined application of Nernst-Einstein equation and conductivity theory is used to characterize the non-saturated chloride diffusivity in cementitious materials.

2.1. NERNST-EINSTEIN EQUATION

Nernst-Einstein equation, i.e. Eq. (1), gives that the ratio of the bulk conductivity of pore solution σ_p to the conductivity of cementitious material σ_{mat} [S/m] is equal to the ratio of chloride diffusivity in the pore solution D_p to the effective chloride diffusivity in cementitious material D_{mat} [m^2/s]. This ratio is defined as formation factor F_0, which is a global factor representing the microstructure of cementitious material. D_p depends on the chloride concentration and is around 1.5×10^{-9} m^2/s at room temperature when the chloride concentration is in the range of 0.1~1.0 mol/l [4]. After obtaining σ_p and σ_{mat}, the effective chloride diffusivity in cementitious material D_{mat} can be calculated. Note that the calculated D_{mat} excludes the chloride binding effect.

$$F_0 = \frac{\sigma_p}{\sigma_{mat}} = \frac{D_p}{D_{mat}} \tag{1}$$

2.2. CONDUCTIVITY OF CEMENTITIOUS MATERIAL $\boldsymbol{\sigma_{mat}}$

The conductivity of cementitious material σ_{mat} is the inverse of its resistivity ρ_{mat} [Ω·m], which is a function of geometry *m* (*m=1* for cylinder sample), length *L* [m], cross sectional area *A* [m^2] and electrical resistance R_{mat} [Ω], as Eq. (2). For a direct current, the electrical resistance of cementitious material (R_{mat}) is determined by Ohm's law and equal to the ratio between applied voltage (U) and direct current (I), as $\mathrm{R}_{mat} = \mathrm{U/I}$.

$$\sigma_{mat} = \frac{1}{\rho_{mat}} = \frac{mL}{A} \cdot \frac{1}{R_{mat}} \tag{2}$$

In general, cementitious material is a three-phase system consisting of solid phase, pore solution phase and vapour phase. Figure 1 illustrates a simple model of cementitious material made of different phases in parallel layers. The parameters R_s (A_s), R_p (A_p) and R_v (A_v) are noted as the electrical resistances (cross sectional areas) of the solid phase, the pore solution phase and the vapour phase layers, respectively. The total resistance of cementitious material (R_{mat}) is related to the resistance of each phase layer, i.e. Eq. (3). Incorporating Eq. (2) into Eq. (3) gives the expression of conductivity, i.e. Eq. (4). Parameters σ_s, σ_p and σ_v are conductivities of the solid phase, the pore solution phase and the vapour phase layers, respectively. σ_{mat} and A_{mat} are the total conductivity and the total exposure surface area of the material. A_{mat} is the summation of the cross sectional area of all layers, i.e. $A_{mat} = A_s + A_p + A_v$.

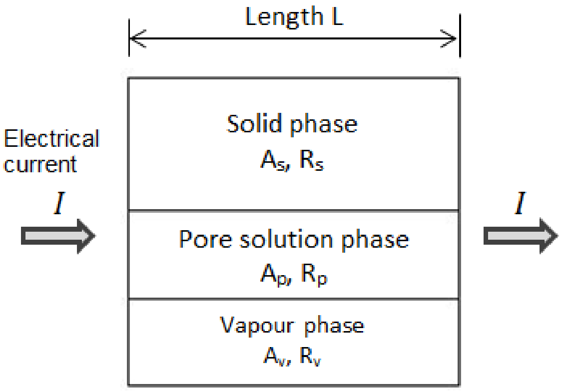

Figure 1: Cementitious material composed of different phases in parallel layers. R_i and A_i respectively represent electrical resistance and cross sectional area of each phase layer

Multiplying both sides of Eq. (4) with material length *L* produces Eq. (5). If the volume fraction of each phase is defined as $\phi_i = V_i/V_{mat}$, then Eq. (6) is deduced. Given the fact that the different phases in cementitious material are not completely in parallel layers [5], a structure factor β_i is introduced that indicates the connectivity of each phase layer and thus Eq. (7) is written. Since the conductivity of pore solution σ_p (1~20 S/m) is usually several orders of magnitudes higher than that of solid phase σ_s (10^{-9} S/m) and vapor phase σ_v (10^{-15} S/m) [4], the total conductivity of cementitious material σ_{mat} is almost equal to the conductivity of pore solution phase layer, i.e. Eq. (8).

$$\frac{1}{\mathrm{R}_{mat}} = \frac{1}{R_s} + \frac{1}{R_p} + \frac{1}{R_v} \tag{3}$$

$$\sigma_{mat}A_{mat} = \sigma_s A_s + \sigma_p A_p + \sigma_v A_v \tag{4}$$

$$\sigma_{mat}V_{mat} = \sigma_s V_s + \sigma_p V_p + \sigma_v V_v \tag{5}$$

$$\sigma_{mat} = \sigma_s \phi_s + \sigma_p \phi_p + \sigma_v \phi_v \tag{6}$$

$$\sigma_{mat} = \sigma_s \phi_s \beta_s + \sigma_p \phi_p \beta_p + \sigma_v \phi_v \beta_v \tag{7}$$

$$\sigma_{mat} \approx \sigma_p \phi_p \beta_p \tag{8}$$

At saturated condition (S_w =100%), the volume fraction of pore solution phase ϕ_p is equal to total porosity of the cementitious material ϕ_t (i.e. $\phi_p = \phi_t$). The structure factor of pore solution phase β_p can be indicated by the connectivity of pores present in the material (η_p). Then Eq. (8) is rewritten as Eq. (9). Here, $\sigma_{mat,Sat}$ is the conductivity of saturated cementitious material and $\sigma_{p,Sat}$ is the conductivity of saturated capillary pore solution.

$$\sigma_{mat,Sat} \approx \sigma_{p,Sat} \cdot \phi_t \cdot \eta_p \tag{9}$$

At unsaturated condition (S_w<100%), the volume fraction of pore solution phase ϕ_p is ($\phi_t S_w$). The structure factor β_p depends upon continuously water-filled pore channels, which are not only related to pore connectivity (η_p) but also affected by water continuity (η_{w,S_w}). Herein water continuity (η_{w,S_w}) is introduced to indicate the connectivity of pore solution phase present in the pore structure ($\eta_{w,S_w} = 0{\sim}1$) and it can be calculated as the ratio between the number of transport pore channels available for ionic diffusion at particular S_w and that at saturated state. Then Eq. (8) is replaced by Eq. (10). Here σ_{mat,S_w} and σ_{p,S_w} are non-saturated conductivities for cementitious material and pore solution, respectively.

$$\sigma_{mat,S_w} \approx \sigma_{p,S_w} \cdot \phi_t S_w \cdot \eta_p \eta_{w,S_w} \tag{10}$$

In unsaturated state, moisture tends to occupy the pores from small size to large size. Therefore, η_{w,S_w} is intimately related to the fineness of pore size distribution. According to Mercury Intrusion Porosimetry (MIP) technique, pore size in hydrated cementitious materials is usually towards to Gaussian distribution [6]. Then η_{w,S_w} and pore structure can be approximately correlated by Gaussian function as shown in Eq. (11), where a parameter c is introduced which is determined by fineness of pore size distribution. If the fineness of pore size distribution is simply indicated by the average pore diameter $d_a = 4V_t/S_t$, where V_t (m^3) and S_t (m^2) are the total volume and total surface area of the pores present in the pore structure, then parameter c shall be a function of d_a, as c= $f(d_a)$. The specific expression of $f(d_a)$ will be further determined afterwards in this paper.

$$\eta_{w,S_w} = e^{-\frac{(1-S_w)^2}{2\cdot c^2}} \tag{11}$$

2.3. RELATIVE CHLORIDE DIFFUSIVITY IN UNSATURATED CEMENTITIOUS MATERIALS

As defined, the relative chloride diffusivity of cementitious material, D_{rc}, is calculated as the ratio of chloride diffusivity at a given S_w level (D_{mat,S_w}) over that at saturated condition ($D_{mat,Sat}$). By using Nernst-Einstein equation, i.e. Eq. (1), the D_{rc} can be calculated based on conductivity measurements (Eq. (12)). Meanwhile, once combining Eq. (1) with Eqs (9)-(11), D_{rc} can be also deduced from analytic model as shown in Eq. (13).

$$D_{rc} = \frac{D_{mat,S_w}}{D_{mat,Sat}} = \frac{\sigma_{mat,S_w}}{\sigma_{mat,Sat}} \cdot \frac{\sigma_{p,Sat}}{\sigma_{p,S_w}} \tag{12}$$

$$D_{rc} = \frac{D_{mat,S_w}}{D_{mat,Sat}} = S_w \cdot \eta_{w,S_w} = S_w \cdot e^{-\frac{(1-S_w)^2}{2\cdot c^2}} \tag{13}$$

In Eq. (12), σ_{mat,S_w} and $\sigma_{mat,Sat}$ are measured directly from conductivity test. σ_{p,S_w} and $\sigma_{p,Sat}$ are related to the pore solution chemistry which may differ with varying S_w. They will be discussed in section 5.1. The measured D_{rc}-S_w relation from Eq. (12) will be fitted by Eq. (13) in order to examine the efficiency of analytic model; at the meantime, parameter c for various mixtures can be obtained.

3. EXPERIMENTAL PROGRAM: MATERIALS, SAMPLES AND TESTS

The raw materials for this study were ordinary Portland cement (OPC) and supplementary cementitious materials (SCMs) such as fly ash (FA), ground granulated blast furnace slag (GGBFS) and limestone powder (LP). Six different binders were designed. The mixture proportions are shown in table 1. Both cement pastes and mortars were cast. One-year cured paste samples were prepared for pore structure measurement, which was performed by MIP technique [6]. One-year cured mortar samples were prepared for conductivity test and pore solution chemistry test.

Cylindrical mortars (ϕ100×800 mm) were cast for conductivity test. After one-year curing, both the top and bottom surfaces of mortar slices with 15 mm thick were cut off. The middle part (50 mm thick) was preconditioned to reach target S_w (ranging 18-100%) and homogeneous moisture distribution. Conductivity test was conducted on all the well-prepared mortar specimens with S_w in the range of 18-100%. Details of sample preconditioning procedures in obtaining well-prepared unsaturated mortar samples and details of conductivity test can be found in previous work [7]. For pore solution chemistry test, one-year moist-cured cylinder mortars (ϕ50×100 mm) were compressed under oil pressure machine (max. capacity 2000 MPa). The compressed pore solutions were collected and stored in plastic bottles, which were considered as the pore solutions of mortar specimens at saturated condition. The concentrations of alkalis (e.g. Na^+, K^+) were tested by means of inductively coupled plasma optical emission spectrometers (ICP-OES).

Table 1: Mixture proportions (weight percentage) used for binders

Mixtures	Type of cement and replacement by weight				Water/binder ratio
	OPC	FA	GGBFS	LP	
P4	100%	-	-	-	0.4
P5	100%	-	-	-	0.5
P6	100%	-	-	-	0.6
PF5	70%	30%	-	-	0.5
PB5	30%	-	70%	-	0.5
PBL5	25%	-	70%	5%	0.5

4. EXPERIMENTAL RESULTS

Based on measured conductivity, the relative chloride diffusivities (D_{rc}) at various water saturations (S_w) were derived following Eq. (12). Figure 2a plots the results of D_{rc}-S_w relation in OPC mortar specimens with water-cement (w/c) ratio of 0.4, 0.5 and 0.6. For a comparative study, the data from previous literature [4] are also present which exhibit consistency to the results obtained in this work. As indicated, D_{rc} decreases as S_w reduces. The most significant drop in D_{rc} is observed when S_w decreases from 90% to 60%. When S_w is below 60%, the D_{rc} is less than 10 % regardless of w/c. The D_{rc} is approaching to zero when the values of S_w are 37%, 28% and 22% for the specimens with w/c increasing from 0.4 to 0.6, respectively.

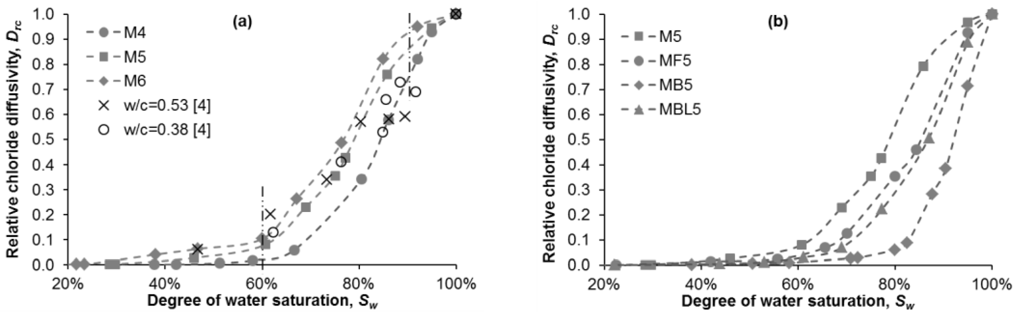

Figure 2 Experimental relationships between D_{rc} and S_w in OPC (a) and blended (b) mortars

Figure 2b shows the effect of SCMs, i.e. FA, GGBFS and LP, on the relationship between D_{rc} and S_w. As indicated, at a given S_w the mortars containing FA or GGBFS exhibit much lower D_{rc} compared to the reference OPC mortar M5. For example at $S_w=80\%$, the D_{rc} is approximately 10% for MB5, 30% for MBL5 and 35% for MF5, while D_{rc} is as high as 60% for the reference sample M5. It is thus deduced from Eq. (13) that the addition of SCMs has great potential in affecting the water continuity in cementitious systems. According to cementing type, the capability in reducing water continuity presents a descending order as GGBFS, FA and OPC.

5. DISCUSSIONS

5.1. CONDUCTIVITY OF PORE SOLUTION $\boldsymbol{\sigma_p}$

In cementitious materials, conductivity of pore solution σ_p is mainly related to the concentrations of alkalis (Na^+, K^+) and hydroxide (OH^-). In this work, the pore solutions of various mortar specimens at *S_w=100%* were squeezed and collected. The concentrations of alkalis (Na^+, K^+) were tested by ICP-OES. The concentration of OH^- was calculated as the sum of alkali concentrations [8]. In general, the released alkalis during cement hydration are either bound by hydrates (mainly C-S-H) or freely present in pore solution. Chen and Brouwers [9] proposed an updated method that can be used to determine the relationship between bound and free alkalis content. The method was applied in this work to predict the alkalis concentrations at different S_w levels, i.e. Eqs (14) and (15). Herein, C_{Na} and C_K are concentrations of Na^+ and K^+ at particular saturation S_w in [mol/L]; V_w is the volume [L] of pore solution which linearly relates to S_w and total porosity ϕ_t; m_{C-S-H} is the mass of hydrate C-S-H [kg]; n_{Na}^r and n_K^r are the moles of alkalis released by cement hydration.

$$C_{Na} = \frac{n_{Na}^r}{V_w + 0.45 \cdot m_{C-S-H}} \tag{14}$$

$$C_K \cdot V_w + 0.2 \cdot (C_K)^{0.24} \cdot m_{C-S-H} = n_K^r \tag{15}$$

After obtaining the concentrations of Na^+, K^+ and OH^-, synthetic solutions were prepared by mixing solids (NaOH, KOH) and distilled water in proper proportions according to the calculated C_{Na} and C_K at each S_w level. The conductivities σ_p at various S_w levels were measured on these synthetic solutions. Figure 3 presents the σ_p-S_w relations for various mortar mixtures. It appears that σ_p is nearly two times larger at S_w=30% than that at saturated condition S_w=100%.

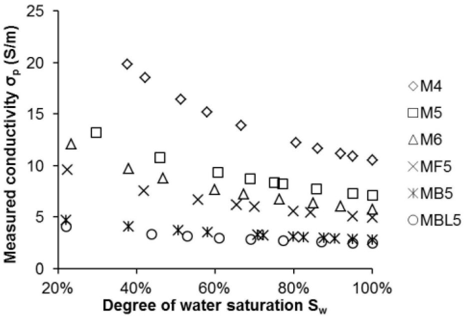

Figure 3 Conductivity of pore solution σ_p against water saturation S_w in mortars made of various cements

5.2. VALIDATION OF ANALYTIC MODEL

In order to examine the efficiency of the analytic model proposed, Eq. (13) is used to fit the measured data as presented in Figure 2b. The fitting curves are given in Figure 4a. It is observed that the Eq. (13) shows good fitness to the experimental results. For further comparison, the proposed model is compared with the current main existing models by examining the fitting goodness on the measured data in this work. Figure 4b shows the curves of three different models by fitting data set of mortar MF5, where the power model is from Buchwald [2] and polynomial model is from de Vera et al. [3]. Amongst the three models, polynomial model yields the poorest fitting that D_{rc} is zero at S_w=57% and thus D_{rc} cannot be fitted at low S_w level (S_w<57%). For power model, the fitting curve deviates greatly from the measured data at high S_w level (S_w>85%). In contrast, the proposed model, i.e. Eq. (13), agrees well with experiments.

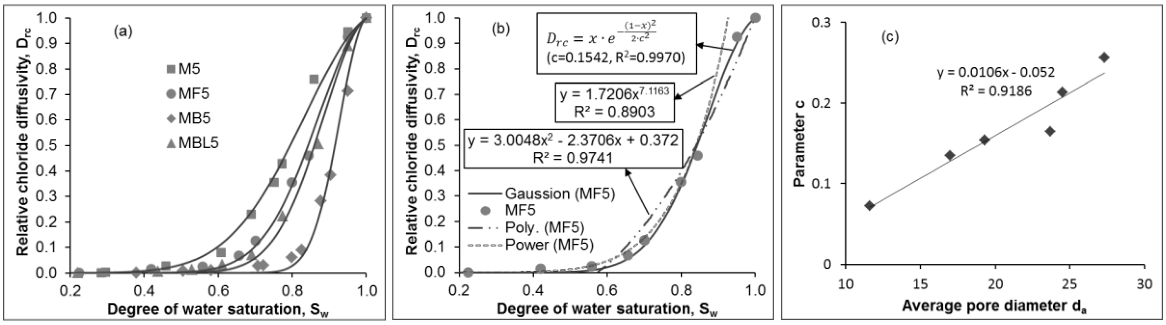

Figure 4 (a) Relationship D_{rc} vs. S_w in various mortar mixtures fitted by Eq. (13); (b) Comparison of various models by fitting plots D_{rc} vs. S_w in mixture MF5; (c) Relationship c vs. d_a for all the tested mixtures

By applying Eq. (13), the values of parameter c for various mortar mixtures are also obtained. According to MIP test, the average pore diameters d_a of corresponding paste mixtures are obtained as well. The relationship between c and d_a is plotted in Figure 4c, which exhibits a linear expression. Accordingly, the water continuity η_{w,S_w} (Eq. (11)) as well as relative chloride diffusivity D_{rc} (Eq. (13)) can be quantified directly in relation to the pore structure. On the other hand, it appears from Figure 4c that at $d_a \approx 5\ nm$, c is approaching to zero, which implies that both η_{w,S_w} and D_{rc} would be predicted as zero when $d_a < 5\ nm$. Conceivably, at $d_a > 5\ nm$, the microstructure contains both capillary pores (> 10 nm) and gel pores (< 10 nm); while at $d_a \leq 5\ nm$, there may be no capillary pores but only gel pores present in the microstructure, in this case the chloride diffusion is negligible [10].

Consequently, the effective chloride diffusivity in unsaturated cementitious material D_{mat,S_w} can be described as:

$$D_{mat,S_w} = D_{mat,Sat} \cdot S_w \cdot e^{-\frac{(1-S_W)^2}{2\cdot(0.0106 d_a - 0.052)^2}} \qquad (d_a > 5\ nm) \tag{16}$$

$$D_{mat,S_w} = 0 \qquad (d_a \leq 5\ nm) \tag{17}$$

where, $D_{mat,Sat}$ is effective chloride diffusivity at saturated state, S_w is water saturation and d_a is average pore diameter of the cementitious material.

6. CONCLUSIONS

In this paper, a new analytic model that characterizes the chloride diffusivity in unsaturated cementitious materials is developed based on the conductivity theory and Nernst-Einstein equation. This model specifies that the effective chloride diffusivity in unsaturated cementitious materials is a function of effective chloride diffusivity in saturated state, water saturation and average pore diameter of the material. The analytic model shows good agreement with the experimental results. Improvement to this analytic model, such as using a more accurate expression correlating the parameter c and pore structure information, is possible.

ACKNOWLEDGMENTS

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