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Analysis of Chloride Diffusivity in Green Concrete Based on Fick’s Second Law

H. Abbaslou*, E. Delnavaz, A. R. Ghanizadeh

Civil Engineering Department, Sirjan University of Technology, Sirjan, Iran

ABSTRACT: The important factor that plays a significant role in preventing the entry of destructive elements into concrete is the cementitious composition of concrete. Moreover, reuse of agricultural wastes in concrete which called green concrete can replace materials used in the manufacturing of concrete and also reduce the negative effects on the environment, such as reduction of waste disposal and CO_2 emissions. In this study, green concrete was produced with ash of Horsetail plant and Rice Husk residues containing a large amount of silicon as an additive with 0, 5, 10, 15, 20 and 25%, replacing Portland cement in four different concrete mix designs. In order to investigate chloride penetration after concrete curing, the specimens were exposed to salinity levels of 0.7, 15 and 35 dS/m from one surface for 150 days with a 10 cm water head. In terms of concrete strength, the optimum percentage of plant ash was 15%. The results showed the trend diffusion coefficient of conventional concrete > green concrete- Horse-tail ash> green concrete-rice husk ash. Thus, green concrete, in addition to the appropriate strength specifications and reduction of environmental problems, also has a major role in the reduction of chloride ion penetration into areas exposed to solutions containing chloride ions.

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1- Introduction

The growing demand for construction all over the world has led to increased usage of concrete, whereas, conventional concrete materials are not fully environmentally friendly [1]. Green concrete is a kind of concrete produced from recycled materials with the aim of preserving nature and reducing energy consumption. Construction in a natural way is a constructional method with short-term economic considerations, while a sustainable construction focuses on the life cycle remarks of a project with a focus on its cost and durability. However, stable construction focuses on the considerations of the life cycle in the project and its cost and durability [2].

Thus far, comprehensive studies have been carried out on utilizing agricultural waste materials such as date palm, coconut, and sugarcane as well as rice husk. Results indicate that these materials have potential for use in concrete. The reuse of agricultural waste materials in concrete could reduce the dependency on conventional concrete-making materials as well as minimize the negative impacts on the environment besides ensuring waste conservation and reduction in waste disposal from these sectors. Although usage of agricultural waste materials results in the reduction of some concrete properties, it is considered as a new method for selecting waste materials to make concrete with ameliorated performance [1].
Moreover, it is well-established that reinforced concrete is susceptible to attacks from seawater, which contains both chloride and sulfate that cause corrosion to this concrete [3]. Chloride ingress is one of the major problems in concrete durability. Most coastal structures are damaged due to chloride penetration and corrosion of concrete meshes. Chloride penetration is one of the major causes of reinforced concrete deterioration [4]. Ion diffusion mechanism due to concentration gradient is considered as a dominant mechanism among the various mechanisms for the movement of ions from concrete. The current equations on the basis of Fick’s second law of diffusion considers, modelling the diffusion coefficient (D) as one of the important parameters in this equation although it is a small step, it is effective in the durable design of long term concrete structures in areas that are prone to damage [5]. It appears, however, that the threshold chloride content is not dominated by any one parameter which can provide a simple index for comparing different types of concrete. It is actually a function of steel-concrete interface, concentration of hydroxide ions in the pore solution (pH), electrochemical potential of the steel, binder type, surface condition of the steel, moisture content of the concrete, oxygen availability on the steel surface, electrical resistivity of the concrete, degree of hydration, chemical composition of the steel, temperature, chloride source (mixed-in initially or penetrated into hardened concrete), type of cation accompanying the chloride ion and presence of other species, e.g. inhibiting substances [6].

Several researchers have presented numerical and experimental models for estimating chloride diffusion coefficient in concrete. Saetta et al. [7] examined different effective parameters for chloride ion diffusion coefficient

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*Corresponding author, E-mail: abbaslou@sirjantech.ac.ir in concrete structures located in marine environments, including temperature, moisture flux in transporting dissolved ions through the porous media and even the time of exposing concrete to chloride environment. The chloride diffusion coefficient in concrete in marine environments was obtained as a function of the cement water ratio by Luping and Gulikers [8]. Boulfiza et al. [9] showed that water movement at a crack is very sensitive to its saturation level and chloride ions ingress is also significantly affected by the presence of cracks. They proposed a Simplified Smeared Approach (SSA) to model the chloride ions ingress into the cracked concrete. In this approach, it is assumed that chloride ions ingress into cracked concrete can be approximated using Fick's Second Law of Diffusion.

On the other hand, cement composition is one of the important factors that play a significant role in preventing the entry of destructive elements into concrete. The composition of the concrete mortar influences the structure of the pores and consequently, its resistance to penetration is changed. However, it is noteworthy that in addition to the properties of cement paste, the influence of access to oxygen and sufficient moisture on the corrosion occurrence should not be ignored [10]. One of the strategies to prevent and reduce these damages is by adding materials such as fly ash, blast furnace slag and micro-silica to the concrete mortar. All of these, when properly added in the mix, significantly reduce the penetrability of concrete and increase its resistivity, thereby reducing the rate of corrosion [11]. Replacing plant residue ash as a portion of cement, in addition to reducing the environmental pollution, it may also have positive effects on the durability and strength of the concrete.

With regards to the new green concrete technology and environmental pollution by the ingression of pollutants due to cement production, the use of green concrete has been taken into consideration for the first time. In other words, the use of concrete in saline waters and lands is expanding unavoidably. This study was conducted to assess the processing of green concrete by applying specified amounts of Horse-tail and Rice Husk residues ashes replacing portion of cement, and assessing the performance of Horsetail ash based on its strength as compared to Rice Husk ash, and also to investigate the diffusion of chloride ion in green concrete with different mix designs, to show the effect of various concrete components on chloride ion diffusion. At last, diffusion coefficients in steady diffusion area of concrete by Fick's second law are calculated

2- Methods and materials

2- 1- Concrete Preparation

Since in this study, the effect of plant ash type on the amount of chloride in green concrete was determined, the ratio of plant ash to cement was changed in all the processes of designing and manufacturing the specimens. Hence, other components of the mixing plan were fixed by eliminating their effects on the evaluation criteria. The effects of changes in the amount of ash on the properties of green concrete were evaluated. The detail of suggested mixtures based on available references and previous studies [12-14] are shown in Table 1.

The particle size distribution of aggregate was performed according to the ASTM D421 standard. In this study, anti-sulfate cement was used in all the experiments. Chemical analysis of cement (Table 2) was in accordance with European standard EV197-1 and ASTM C595 standard. In order to investigate the effect of cement, 180, 280, 350 and 400 kg/m^3 of cement factor were used in different mix designs.

Table 1. Concrete mixture designs

Mix ID	Cement (kg/m^3)	Fine Aggregates (kg/m^3)	Coarse Aggregates (kg/m^3)	Cement/Water ratio	Plant Ash (kg/m^3)
Mix-1	280	892	858	0.6	42
Mix-2	180	822	728	0.6	27
Mix-3	350	1088	720	0.6	52.5
Mix-4	400	1207	518	0.6	60

Table 2. Chemical composition of cement (wt. %)

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	LOI
content	62.12	20.68	4.48	4.62	3.11	1.91	0.66	0.37	1.73

LOI: Loss On Ignition

Ash of Horse-tail plant residues and Rice Husk were used for comparison due to their high silica content. To produce plant ashes, Horsetail plant (Equisetum arvense L.) and rice husk, prepared from farms in northern Iran, were used. Horsetail is a perennial plant that is found in or near watery areas such as marshes, streams or rivers. Its reedy exterior and silica content have made it a popular metal polisher and natural abrasive cleanser [15]. Rice husk contains 90-85% silica; when mixed with wind ash and granule furnace slag, as a replacement for porcelain cement, is a very suitable material for concrete production using a carbon dioxide reduction approach [16]. Horsetail plant and rice husk were dried, milled and placed in a furnace at 650 °C for 1 h to become ashes and it was found that these plants lost an average of 75% of their mass in the furnace. Optimum temperature and time were selected based on the research conducted by Khaloo et al. [17]. To determine the ash composition, specimens of the X-ray fluorescence apparatus (PHILIPS-PW1410) were analysed and to investigate the optimal percentage for chloride penetration experiments, a cube specimen of 100 × 100 × 100 mm^3 dimensions with a treatment time of 28 days was prepared from each mixing design (two replications) and an optimum percentage of ash was obtained by measuring compressive strength of concretes containing 0, 5, 10, 15, 20 and 25%, replacing plant ashes with cement. For each mix design, an 8 to 9 cm slump was produced with water to yield concrete strengths in conventional ranges.

2- 2- Coating of concrete specimen

The molds were covered with burlap and kept wet for 24 h after casting. The specimens were removed from the molds and allowed to cure in water saturated for 28 days. Except for 4 cube control specimens, the specimens were painted on five sides with three layers of Bitu Coat W paint such that the solution of sodium chloride entered only from one side (Figure 1).

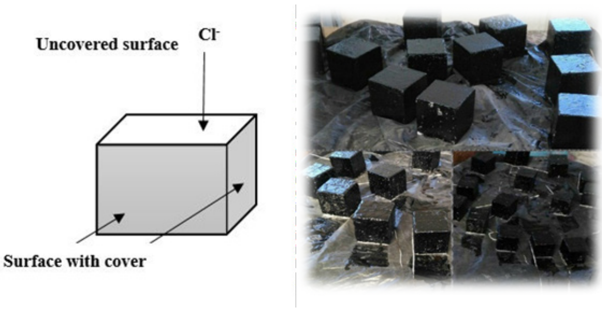

Figure 1. Sealing the concrete by Bitu paint

The specimens were submerged in two baths of sodium chloride solution (EC=15 dS/m, EC=35 dS/m) and a bath of water (EC=0.7 dS/m) for 150 days. During this time, the height and salinity of the water were kept constant. The compressive strength was determined using a fully automatic shutter jack according to the standard (ASTM C109) and loaded at 0.3 MPa/s. The slump of all the samples was considered as 8-10 cm.

2- 3- Preparation of specimens for analysis of the amount of chloride

After an exposure period of 5 months, the specimens were removed from the exposure conditions and dried, then moved to a stone cutter for cutting and sealed from the same 5 sides, 1 cm from each side to accurately measure the amount of chloride intrusion from the surface in the concrete core.

2- 4- Measurement of the amount of chloride

The fine particles from each ground layer (measurement of the amount of chloride showed that penetration is usually up to 5 mm) were collected and analyzed separately to determine the content of acid-soluble chloride according to ASTM C1152 (2003) and ASTM C114 (2003). The eroded surface and powder were obtained to measure chloride and 0.2 g of each layer of a specimen were added to 50 cm^3 of HNO_3 (1:2). When the effervescence has ceased, the suspension was heated with continuous agitation for 1 min until it boiled. 1 cm^3 of the standardized 0.05 M $AgNO_3$ solution was added by means of a pipette. The suspension was allowed to boil for 1 min more and filtered using a filter paper previously washed with HNO_3 (1:100), and the filtrate was put in a 25 cm3 filtration flask. The beaker, agitator and filter paper were adequately washed with HNO_3 (1:100). The final volume of the filtrate was about 10 cm^3. The filtrate was allowed to cool down to room temperature. 4 drops of the indicator solution were added to the filtrate, stirred vigorously and titrated with the 0.05 M NH_4SCN solution. The titration was stopped when a drop of thiocyanate solution produced a slight red-brown color, which did not disappear with agitation. The spent volume (V1) of the NH_4SCN solution was recorded and a blank test was run using the procedure described above with the same reagents but without the sample. The spent volume (V2) of NH_4SCN solution corresponding to the blank test was recorded [18].

The chloride content of the concrete, expressed as percentage relative to the weight of dry specimen (% Cl), was calculated using the following expression (Equation 1):

$$\% CL = \frac{3.5453 V_{Ag} M_{Ag} (V_2 - V_1)}{m V_2} \quad (1)$$

Where, V_{Ag} is the volume of $AgNO_3$ added (in cm^3), MAg is the real molarity of the $AgNO_3$ solution, V_1 and V_2 are the volumes of NH_4SCN solution (in cm^3) used in the specimen and blank tests, respectively, and m is the mass of the specimen portion (in grams).

2- 5- Chloride transport model

The corrosion of steel reinforcement is primarily controlled by the diffusion of chlorides. The effect of hydraulic pressure and capillary sorption was not considered in the model described as in most cases, it can be ignored. Diffusion is thus the most common way in which chloride ions are brought into contact with the reinforced concrete bridges decks. Diffusion occurs as a result of concentration gradients. In other words, if the chloride ions are not evenly distributed in a liquid, the ions move from the area with the highest concentration to the area with a lower concentration. The process continues until the concentrations are evenly distributed.

The process of chloride passage through concrete as a function of depth and time can then be modeled with the aid of Fick's 2nd law of diffusion, as is generally accepted (Equation 2).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} \qquad (2)$$

Where:
C: concentration of ions [%],
z: depth [m] (from the surface subject to chlorides),
t: time [s],
D: diffusion coefficient [m²/s].

The differential formula (Equation 2) can be solved when applying the following boundary conditions.

C (z = 0, t > 0) = C_0, constant concentration of chlorides on the surface C0,

C (z > 0, t = 0) = 0, the initial concentration in concrete is 0,

C (z = ∞, t > 0) = 0, the zero concentration is at infinity.

This is called Cracks solution and was applied to the problem of diffusion in concrete in the work of Collepardi [19] (Equation 3):

$$C_{z,t} = Co\left[1 - \mathrm{erf}\left(\frac{z}{\sqrt{4Dc\,t}}\right)\right] \qquad (3)$$

$$erf(a) = \frac{2}{\sqrt{\pi}}\int_0^a e^{-\beta^2}d\beta \qquad (4)$$

Where:
$C_{z,t}$ is the concentration of chloride ions [%] (expressed as a percentage of all materials with cementation properties) and in time t (years) depth z [m],
C_0 is the concentration of chloride ions (expressed as a percentage of all materials with cementation properties) at the concrete surface [%],
D_c is the effective diffusion coefficient [m²/s],
t is time of exposure [s]
erf is the error function.

A polynomial development can help in the numerical solution to the chosen differential Equation (Equation 5)

$$C_{z,x} = Co\left\{1 - \frac{2}{\sqrt{\pi}}\sum_{n=0}^{14}\frac{(-1)^2\left(\frac{z}{\sqrt{4Dc\,t}}\right)^{2n+1}}{n!\,(2n+1)}\right\} \qquad (5)$$

Equation 3 and its solution (Equation 5) are widely used aids for modeling the penetration of chlorides even though they do not allow the description of the time-dependent changes of material properties or more complicated marginal conditions. When modelling more complicated marginal conditions, it is necessary to use models on the basis of numerical approaches, for instance, finite element methods. Due to the long term curing of concrete, the diffusion coefficient is a time-dependent parameter. Its development over time can be determined using reference values and the curing coefficient [8, 20] (Equation 6):

$$DC(t) = Dc,ref.\left(\frac{tref}{t}\right)^m \qquad (6)$$

In Equation 6,
D_c (t) is effective diffusion coefficient for the chosen age [m²/s],
$D_{c,ref}$ is diffusion coefficient obtained from a referential old structure [m²/s],
T is curing time [years],
tref is reference period for measurement [years] and
m is curing coefficient [-].

For a 1D analysis of a chloride profile during the life of the structure, it is possible to use a relationship developed in relation to Cracks solution [21] (Equation 7):

$$C_{z,t} = Co\left[1 - \mathrm{erf}\left(\frac{z}{\sqrt{4\frac{D_{c,ref}}{1-m}\,t^{(1-m)}}}\right)\right] \qquad (7)$$

Where:
$C_{z,t}$ is the concentration of chloride ions [%] (expressed as a percentage of all materials with cementation qualities) and in time t (years) depth z [m],
C_0 is the concentration of chloride ions (expressed as a percentage of all materials with cementation qualities) at the concrete surface [%],
$D_{c,\,ref}$ is diffusion coefficient obtained in a referential old structure [m²/s],
t is exposure time [s],
m is concrete curing coefficient [-] and
erf is the error function.

2- 6- Calculation of the chloride diffusion coefficient

The apparent chloride diffusion coefficient (D) and the surface chloride concentration (C_s) were determined for each specimen by fitting profiles of chloride concentration versus depth according to Fick's second law of diffusion [22] (Equation 8):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (8)$$

Where, an analytical solution for differential Equation 8 is presented by Crank's solution (Equation 9) [22]:

$$C(x, t) - C_0 = (C_s - C_0)\mathrm{erf}(X/\sqrt{4Dt}) \qquad (9)$$

Where, C_0 is the initial concentration of chlorides. In this study, it was assumed that at the beginning of the test, the initial concentration of chlorides inside the specimen was 0.07 (C_0 = 0.07). The free chloride concentration, depth of penetration, chloride surface concentration (for EC=35 dS/m-C_s= 1.24 and for EC=15 dS/m-C_s= 0.53) and time (t=150 days) of the diffusion test were known, and the diffusion coefficient could be calculated with Equation 9 using MATLAB software.

2- 7- Microscopic studies

Using microscopic methods, high-magnification images can be obtained from the material so that the details can be studied accurately. Concrete compounds were observed using FE-SEM. The microscope used in the study was a FESEM TESCAN MIRA3 microscope. A semi-quantitative chemical analysis was performed using X-ray energy spectroscopy (EDS) for the samples.

3- Results and discussion

3- 1- Concrete Properties

The concrete produced is green due to the presence of pozzolanic material. According to Halakouee and Qaderi [23] and Faghih Maleki et al. [24], pozzolanic materials can be a suitable substitute for cement in concrete, and play an important role in the durability of concrete specimens. As stated, the effect of replacement of different percentages of Horsetail plant and rice husk ashes with cement as artificial pozzolan, on compressive strength and chloride ion penetration in concrete was investigated. The results showed that the optimum percentage of plant ash (rice Husk and horse-tail) was 15% cement replacement and the highest compressive strength in four different concrete mix designs was obtained in this amount of ash (Table 3). With specimens of rice husk ash, Christopher et al. [25] and Bansal & Antil [26] showed that a 10% substitution has a suitable effect while this amount increased by 15% in the studied specimens. Siddique [27] in his research showed that the optimal percentage of volcanic ash in concrete is 20%. It is now widely accepted that there is significant potential for reclaiming and recycling waste materials for use in value-added applications to maximize economic and environmental benefits. Many governments throughout the world have now introduced various measures aimed at reducing the environmental pollution and encouraging reuse and recycling, where it is technically, economically, or environmentally acceptable.

The results showed that active silica in the Horsetail plant ash in the matrix structure of the concrete increased the strength of the concrete. The results of the chemical composition of the rice husk and Horsetail, using the X-ray fluorescence analyzers, are presented in Table 4. According to the results, the percentage of silica oxide for rice husk is more than that of the Horsetail, but the percentage of calcium oxide for Horsetail is more than that of the rice husk.

Scanning electron microscopy (SEM) images of ordinary concrete and green concrete (containing 15% of the Horsetail ash) of mixture 1 are shown in Figures 2 and 3, respectively. Due to the type of cement and concrete compounds, different crystalline images can be seen in the hydrated composition. One of the typical types is C-S-H, calcium hydroxide and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) (Figure 2a).

Table 3. Compressive strength properties of concretes (MPa)

Standard Deviation	Mean	Mix-4	Mix-3	Mix-2	Mix-1	ID
4.50	11.4	16.0	14.2	6.18	9.31	H-15
6.07	13.9	19.4	18.1	6.37	11.6	R-15

H-15: concrete containing 15 % Horsetail ash replacement, R-15: concrete containing 15 % rice husk ash replacement.

Table 4. chemical composition of plant ashes

Amount (wt. %)		Composition
horsetail	rice husk	
60.762	87.998	SiO_2
0.214	0.475	Al_2O_3
0.549	0.741	Fe_2O_3
5.827	1.562	CaO
0.385	0.634	Na_2O
2.799	1.61	MgO
15.313	3.639	K_2O
0.034	0.062	TiO_2
0.022	0.087	MnO
0.943	1.053	P_2O_5
2.152	2	LOI*

*Loss On Ignition

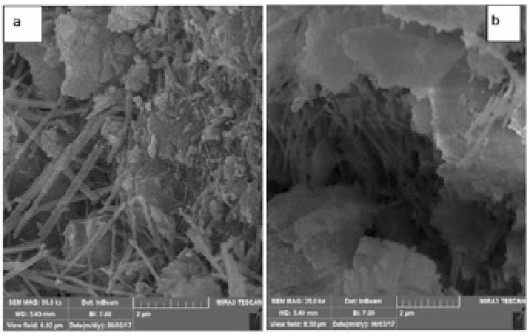

Figure 2. SEM images after 28 days curing of conventional concrete; a) higher magnitude and b) lower magnitude

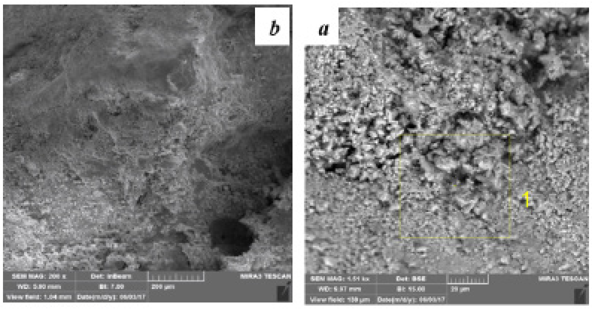

Figure 3. SEM images of green concrete containing 15% ash of Horse-tail plant after 28 days curing: a) higher magnitude and b) lower magnitude

Calcium carbonate amorphous and polycrystals, together with the needle-shaped ettringite crystals (Figure 2b) are also other forms. Scanning electron microscopy images of ordinary concrete (Figure 3) show that ettringite was developed.

Gypsum and ettringite occupy a large amount in comparison with the original products, which as a result, expands and creates cracks in concrete, leading to reduced capacity of the component. Although the formation of gypsum is accompanied by an increase in volume from 1.2 to 2.2, this reaction plays only a minor role in the corrosion process. The reaction between gypsum and calcium aluminate hydrate (C3A) with the formation of ettringite is much more dangerous. The mineral volumes of the ettringite are several times greater than the volume of the initial compounds. Some researchers reported an increase in volume by a factor of 2, while others reported a factor of 7. Thus, the formation of ettringite is the main factor for expansion, which leads to an increase in internal pressure and failure of the concrete matrix. Also, when the concrete is invaded by sulfuric acid, the plaster is deposited in the damaged layer and decreases the ability of the acid to enter the concrete.

Green concrete samples, as compared to conventional concrete, have a denser surface which is porously-lowered, and increases the strength of concrete. SEM images of the Horsetail ash showed that the ash produced is amorphous and because of high silica and calcium, it has pozzolanic and cementitious properties; therefore, it could be a good alternative for cement substitution. An elemental analysis of a concrete specimen containing Horsetail ash presented high amounts of silica and calcium in these samples.

Mostly, green concretes consists of two parts i.e. the use of waste as a substitute for cement and as a substitute for aggregates. In Iran, the most widely used materials in concrete consisting of agricultural wastes, mine tailings, construction debris and glass. Tavakoli et al. [28] emphasized that the consumption of cement is 60 million tons per year in Iran; if 5% of the concrete projects in our country used 10 to 15% of waste material to replace cement, in one year a large amount of the waste generated in Iran can be reused. Also, if this consumption of cement continued and extended to 10% of the country's projects, the total waste from past years can be completely consumed by reusing it in concrete in a few years.

3- 2- Analysis of chloride penetration

The effect of chloride penetration and the amount of ash on chloride diffusion coefficient, in four different cement levels (180, 280, 350 and 400 kg/m^3) and aggregates amounts (1550, 1750, 1800, 1725 kg/m^3) are shown in Tables 5 to 12.

Table 5. Amounts of chloride penetration in concretes containing horsetail ash (mix design 1)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient (10^{-13} × m^2/s)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.433	0.299	2.45	280	0	1750	T-0
0.319	0.19	1.35	266	14	1750	H-5
0.274	0.156	1.07	252	28	1750	H-10
0.345	0.213	1.55	238	42	1750	H-15
0.341	0.210	1.52	224	56	1750	H-20
0.37	0.236	1.76	210	70	1750	H-25

T: Conventional Concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 6. Amounts of chloride penetration in concretes containing rice husk ash (mix design 1)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient (10^{-13} × m^2/s)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.433	0.299	2.45	280	0	1750	T-0
0.296	0.173	1.21	266	14	1750	R-5
0.266	0.15	1.03	252	28	1750	R-10
0.417	0.282	2.24	238	42	1750	R-15
0.304	0.179	1.26	224	56	1750	R-20
0.325	0.196	1.40	210	70	1750	R-25

T: Conventional Concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 7. Amounts of chloride penetration in concretes containing horsetail ash (mix design 2)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.472	0.341	3.03	180	0	1550	T-0
0.453	0.32	2.72	171	9	1550	H-5
0.349	0.217	1.58	162	18	1550	H-10
0.449	0.316	1.67	153	27	1550	H-15
0.482	0.353	3.21	144	36	1550	H-20
0.485	0.356	3.27	135	45	1550	H-25

T: conventional concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 8. Amounts of chloride penetration in concretes containing rice husk ash (mix design 2)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.472	0.341	3.03	180	0	1550	T-0
0.421	0.286	2.29	171	9	1550	R-5
0.438	0.304	2.51	162	18	1550	R-10
0.319	0.19	1.35	153	27	1550	R-15
0.355	0.222	1.62	144	36	1550	R-20
0.330	0.200	1.43	135	45	1550	R-25

T: Conventional Concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 9. Amounts of chloride penetration in concretes containing horsetail ash (mix design 3)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.383	0.248	1.88	350	0	1800	T-0
0.494	0.366	3.44	332.5	17.5	1800	H-5
0.527	0.404	4.18	315	35	1800	H-10
0.395	0.26	2	297.5	52.5	1800	H-15
0.332	0.202	1.45	280	70	1800	H-20
0.429	0.295	2.39	262.5	87.5	1800	H-25

T: conventional concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 10. Amounts of chloride penetration in concretes containing rice husk ash (mix design 3)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.383	0.248	1.88	350	0	1800	T-0
0.395	0.26	2	332.5	17.5	1800	R-5
0.355	0.222	1.62	315	35	1800	R-10
0.256	0.143	0.97	297.5	52.5	1800	R-15
0.246	0.137	0.92	280	70	1800	R-20
0.36	0.227	1.67	262.5	87.5	1800	R-25

T: conventional Cconcrete, R: concretes containing rice husk ash, number: percentage of cement replacement

Table 11. Amounts of chloride penetration in concretes containing horsetail ash (mix design 4)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.377	0.242	1.82	400	0	1725	T-0
0.339	0.208	1.50	380	20	1725	H-5
0.442	0.308	2.56	360	40	1725	H-10
0.400	0.265	2.05	340	60	1725	H-15
0.382	0.248	1.87	320	80	1725	H-20
0.324	0.195	1.39	300	100	1725	H-25

T: conventional concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Table 12. Amounts of chloride penetration in concretes containing rice husk ash (mix design 4)

Chloride concentration amounts (X=5 mm, t=12 months) (%)	Chloride concentration amounts (X=5 mm, t=6 months) (%)	chloride Diffusion coefficient ($10^{-13} \times m^2/s$)	Cement	Ash	Aggregate	ID
			kg/m^3			
0.377	0.242	1.82	400	0	1725	T-0
0.231	0.127	0.85	380	20	1725	H-5
0.253	0.141	0.96	360	40	1725	H-10
0.253	0.141	0.96	340	60	1725	H-15
0.330	0.200	1.43	320	80	1725	H-20
0.253	0.141	0.96	300	100	1725	H-25

T: conventional concrete, H: concretes containing horsetail ash, number: percentage of cement replacement

Replacing different percentages of Horsetail plant and Rice Husk ashes with cement as natural pozzolan shows a change in the chloride diffusion coefficient. Increasing the depth from the concrete surface reduces chloride ion penetration in green concrete specimens. In concrete containing ash of Horsetail plant, the amount of penetration (1 to 2 mm) is higher than that of the concrete containing Rice Husk ash.

The results showed that in the mix design 1, increase in the percentages of both types of ash, reduced this coefficient. This coefficient is lower in specimens containing rice husk ash in comparison with the Horsetail and control specimens. The lowest diffusion coefficient was observed in10% plant ash replacement (Figure 4).

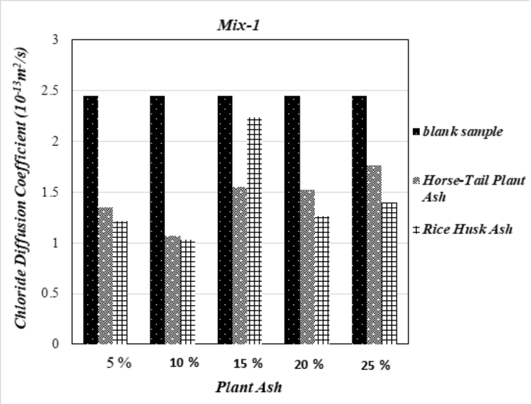

Figure 4. Variations of chloride ion diffusion coefficient (mix design 1)

Based on the results of the mix design 2, an increase in the percentages of rice husk ash reduced this coefficient. This reduction was observed in specimens containing Horsetail ash with up to 15% cement replacement as compared to the control specimen. This coefficient is lower in specimens containing rice husk ash in comparison with the horse-tail and control specimens. The optimal percentage of Horse-tail ash specimens is 10% and the optimal percentage of Rice Husk ash specimens is 15% based on the lowest diffusion coefficient (Figure 5).

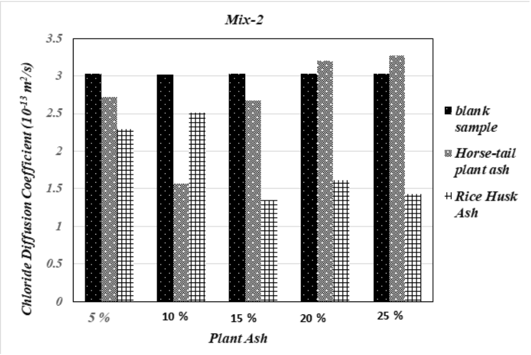

Figure 5. Variations of chloride ion diffusion coefficient (mix design 2)

In mix design 3, adding different percentages of both types of ashes showed different variations in the diffusion coefficient, so that in the specimen containing 5% rice husk ash, the highest coefficient was observed, and in the specimen containing 10% Horsetail ash, the highest diffusion coefficient was observed. However, this coefficient in the specimens containing ash of rice husk decreased more than that of the Horsetail ash and control sample. Also, the optimum percentage of replacing ash was observed in the specimens containing 20% plant ashes (Figure 6)

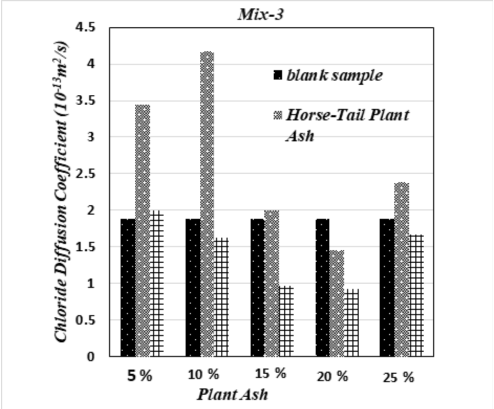

Figure 6. Variations of chloride ion diffusion coefficient (mix design 3)

In mix scheme 4, addition of different percentages of both types of ashes showed different variations in the diffusion coefficient, so that in the specimen containing 20% of rice husk ash, the highest coefficient was observed and in the specimen containing 10% of Horsetail ash, the maximum diffusion coefficient was observed. However, this coefficient in the specimens containing ash of rice husk decreased more than that of the Horsetail ash and control sample. Also, the optimum percentage of plant ashes was 20% for concretes containing Horsetail ash and 5% for specimens containing rice husk ash (Figure 7).

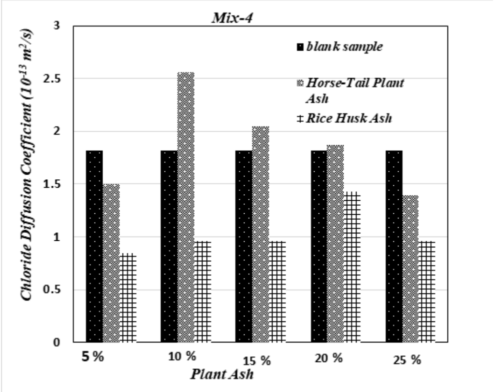

Figure 7. Variations of chloride ion diffusion coefficient (mix design 4)

As shown, in the four mix designs, green concrete specimens containing rice husk ash showed the least amount of chloride diffusion coefficient as compared to Horsetail ash. The lower the percentage of coarse aggregates, with a greater percentage of plant ash, the lower the diffusion coefficient. The higher diffusion coefficient expected with the greater porosity values and the lower cement contents.

Farahani et al. [29] presented an empirical model in accordance with the second law of Fick propagation and linear analysis of regression in concrete with methacetylene replacement with cement. Their results showed that an increase in the percentage of methacoalene replacement was effective in reducing the amount of chloride ion released in concrete, and the coefficient. The diffusion coefficient of concrete was decreased over time and was increased with increasing temperature.

Ehlen [30] also considered the diffusion coefficient of ion chloride in concrete containing Portland cement as a function of time of confrontation in the chloride medium and the concrete sample temperature and calculated the chloride diffusion coefficient in concrete containing silica soot. There is a good correlation between the porosity of fresh concrete and chloride diffusion coefficient under experimental conditions. On the other hand, the chloride diffusion coefficient can be calculated using the porosity of concrete [31].

Song et al. [32] modeled chloride diffusion in concrete immersed in $CaCl_2$ and NaCl solutions. They concluded that the total chloride concentrations of the concrete specimens immersed in $CaCl_2$ solution are much higher than that of the specimens immersed in NaCl solution. The difference in the free chloride profiles of the concrete specimens immersed in $CaCl_2$ and NaCl is much smaller than that of the total chloride profiles. This indicates that the difference between the chloride diffusion behaviors of the specimens immersed in the two source solutions mainly resulted from chloride-binding. So, based on the concentration of free chloride, there is no significant difference between the two solutions ($CaCl_2$ and NaCl).

The results of Chloride Diffusivity Analysis of Existing Concrete based on Fick's Second Law by Junzhi et al. [30] revealed that under natural chloride environment, the maximum chloride concentration in existing normal hydraulic concrete is not on the concrete surface. For chloride ions content, at 1-2 cm depth towards the surface, it is generally unsteady, but steady diffusion area is located at 2 cm depth behind the concrete surface after 37 years. There is a strong linear relationship between the depths of controlling beginning points of steady diffusion area with porosity of concrete. They calculated mean chloride diffusion coefficients for different reinforced concretes and the values of 0.8×10^{-13} to 2.3×10^{-13} m^2/s was achieved.

4- Conclusion

In this research, the effect of Horsetail and rice husk ashes on chloride ion diffusion was investigated and the following results were obtained:

1. The performance of concrete with cement replacement by plant residue ashes (Rice Husk Ash and Horse-Tail) is outstanding considering compressive strength and resistance to water and chloride ion penetrations which are in many cases the most important characteristic concerning durability, corrosion prevention and enhancing sustainable development by natural replacing materials.
2. The optimum percentage of plant ashes with regards to concrete compressive strength was 15% replacement with cement in different mix designs.
3. Although, rice husk which is an additive substitute for cement has been introduced by researchers as a very suitable material for producing concrete with an approach of carbon dioxide reduction, the results of this study showed that Horsetail plant ash can also be used as a green material in concrete and cement industries due to its high Si and Ca levels.
4. Adding the plant's ash increased surficial chloride amounts. This phenomenon was observed in all the specimens and this can be due to the fact that the addition of plant ash improves the microstructure of concrete and chloride ion can hardly penetrate into the concrete, making the ion to be accumulated in the concrete shell.
5. With the addition of ash in both concrete types, the chloride diffusion coefficient decreased as compared to the control specimen. The lowest diffusion coefficient was calculated for concretes containing rice husk ash substitutes. The chloride diffusion coefficient in conventional concrete changed at a range of 1.82×10^{-13} to 3.03×10^{-13} m^2/s, in concrete containing 15% of Horsetail ash, the range was 1.55×10^{-13} to 2.02×10^{-13} m^2/s and in concrete containing 15% rice husk ash, the range was 0.96×10^{-13} to 2.24×10^{-13} m^2/s.
6. Reducing the diffusion coefficient among different mixing designs showed that the diffusion coefficient has a direct relationship with the amount of cement and an inverse relation with porosity values. Therefore, any factor that increases the strength of the concrete will have a positive impact on the reduction of the diffusion coefficient.
7. The diffusion coefficient data helps in predicting the influence of chloride at different times. In general, green concrete has a positive effect on the reduction of chloride penetration.
8. The replacement of concrete cement portion by waste materials and by-products gives an opportunity to manufacture economical and environment-friendly concrete. However, Horsetail due to numerous medical applications is expensive and less economic.

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