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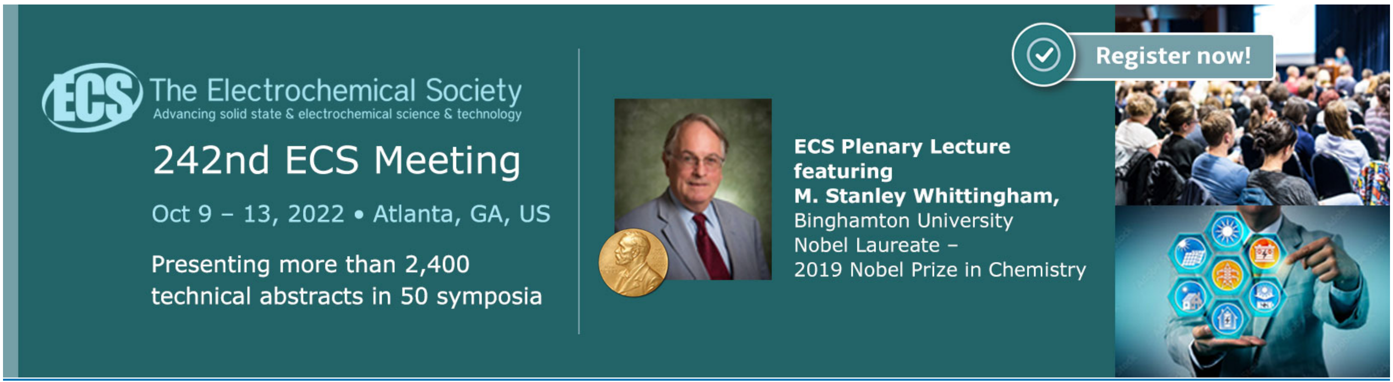

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Performance of nano metaclay on chloride diffusion for ultra- high performance concrete

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Abstract. The major cause for corrosion of steel reinforcement embedded in concrete due to chloride penetration has been the great research effort. The use of nano metaclay in UHPC increase the strength and helps the formation of micro pores by acting as a filler thus improve the chloride penetration resistance characteristic. The aim of this study is to evaluate the chloride diffusion of UHPC using RCPT and chloride penetration depth. Four (4) series of UHPC comprised of plain UHPC and a series of nanoUHPC incorporating 1%, 3% and 5% of nano metaclay were produced. It is reported that the compressive strength of nanoUHPC1 exhibits higher strength up to 10% compared to plain UHPC. The results showed that UHPC containing nano metaclay also significantly affect the chloride diffusion coefficient. As regards to the results, inclusion of 1% nano metaclay in UHPC led to noticeable benefit towards strength and chloride resistance.

1. Introduction

Corrosion of steel embedded in concrete is the major cause of deterioration of reinforced concrete structure, especially chloride is the main causes of steel corrosion. Due to novelty of ultra-high performance concrete (UHPC), this category of concrete exhibits enhanced durability properties and shows great potential towards chloride resistance properties. L'Hôpital et al. [1] disputed that chloride ions pass easily through the diffusion layer of the C-S-H. This finding should be underlining the needs to further improvement to assess the chloride resistance of concrete. One of the commonly parameter to be considered is chloride diffusion coefficient which is mainly affected by the pore structure [2,3]. The chloride coefficient of diffusion can be defined as the capacity of concrete to resist the chloride penetration [4]. The use of low w/c ratio and inclusion of mineral additive such as silica fume, fly ash, slag, ground granulated blast furnace slag and clay have strong relationship in reduction of chloride diffusion coefficient characteristic [5-8]. However, Justnes et al. [9] revealed that the chloride diffusion coefficient was found that increases the content of additive as cement replacement in concrete did not improve the chloride diffusion. Dobias et al. [10] remarked that the chloride diffusion in UHPC has lowest permeability as compared to those of normal concrete (NC) and high-performance concrete (HPC). Another researcher [11] asserted that the chloride diffusion coefficient of UHPC is 30 to 600 times smaller than those of NC and HPC. This might be explained due to large amount of ultrafine particles and superplasticiser dosage resulting low permeability due to very homogenous, compacted and dense pastes. The use of mineral admixture also improves the chloride penetration resistance of UHPC [12].

As well-known, silica fume goes through high pozzolanic reactivity to form additional C-S-H gel in UHPC thus can have nucleation effect at early age of UHPC [13]. Silica fume provides denser particles to UHPC and lower its chloride penetration. Similarly, Tafraoui et al. [14] also found that the UHPC containing metakaolin enhances the chloride diffusion coefficient. Another researcher [15] expressed the opinion that partial replacement up to 7% of silica fume in concrete reduces the diffusion coefficient whereas for higher replacement does not improve the diffusion coefficient. The numerical simulation on the relationship between w/c ratio, components of mix design and duration of immersion reflect to chloride diffusion coefficient was conducted by past researcher [16,17]. They also exemplified that the chloride diffusion in concrete is strongly dependent to those of parameters. Abbas et al. [18] also summarised that the chloride diffusion in UHPC is highly dependent on the exposure solution, duration, w/c ratio and curing regime. It has been shown that the chloride diffusion coefficient of UHPC is significantly lowered than those of NC and HPC.

The most popular techniques on non-steady state chloride diffusion tests have been employed to assess the chloride coefficient of diffusion for concrete such as salt ponding test (AASTHO T259) and bulk diffusion test (NTBUILD 443). In order to offer an alternative to standard, several researchers have proposed a new procedure for calculating the chloride diffusion coefficient consists of an experimental by determination of the electrical current using rapid chloride permeability test (RCPT) [19,20]. Generally, RCPT is a method to evaluate the resistance of concrete to chloride ions ingress through electrical conductivity quantities called as Coulombs. Baasuoni et al. [19] believed that there is a need to obtain a multiple measurement such as chloride penetration depth from the RCPT which better correlates to evaluate the chloride diffusion of concrete. In this present paper, an alternative method proposed by previous researchers have been adopted to determine the chloride diffusion coefficient of UHPC incorporating different levels of calcined nano clay (nano metaclay) content.

2. Experimental Programme

2.1 Materials

Four (4) concrete mixtures of ultra-high performance concrete (UHPC) with water to cement ratio (w/c) of 0.20 were prepared. The mixtures were divided into two (2) groups namely UHPC produced from ordinary Portland cement (OPC) and UHPC partially replaced with calcined nano clay. A series of NanoUHPC comprised of 1%, 3% and 5% from the total weight of OPC used and labeled as NanoUHPC1, NanoUHPC3 and NanoUHPC5, respectively. The basic components of cement, coarse aggregate, sand, water and superplasticiser were mixed together by using dry mix method. The size of crushed gravel aggregate passing with size of 10 mm was used. For sand, it passes through 4.5 mm and predominantly retained on the 60 μm sieve. The commercially available nano clay powder (hydrophilic bentonite) was procured from Sigma-Aldrich (M) Sdn. Bhd. The raw nano clay samples were underwent heated treatment at the temperature of 700°C for 3 hours to formed calcined nano clay (nano metaclay). The calcination process is required for making the nano clay samples become reactive thus can react chemically with traditional cement. The chemical composition of the OPC, nano clay and nano metaclay are listed in Table 1. It is shows that the content of silica (SiO_2) for nano metaclay was highest as compared to those of OPC and nano clay. Almost 66% of SiO_2 is recorded for nano metaclay thus confirmed the potential of strength increment when blending with OPC itself. The content of alumina oxide (Al_2O_3) for nano metaclay is also 80% highest compare to OPC. Highest content of Al_2O_3 can be influenced the hydration process in cement bonding. It can be concluded that nano clay after underwent the calcined process become reactive pozzalannic material as compare to OPC due to highest production of SiO_2 and Al_2O_3. On the other hand, the targeted slump for fresh concrete was fixed to 120 mm for each mix to determine the workability of fresh UHPC. Therefore, the amounts of superplasticiser used are different for each series. Table 2 shows the details of each concrete mix design used in this study.

Table 1. Chemical composition of ordinary Portland cement, nanoclay and nano metaclay

Compound (%)	OPC	Nano Clay	Calcined Nano Clay
SiO_2	11.60	63.90	65.90
Al_2O_3	2.20	14.00	15.10
CaO	75.17	4.80	4.30
TiO_2	0.40	1.01	0.90
Fe_2O_3	5.38	13.41	11.40
K_2O	0.43	0.27	0.24

Table 2. Series of mix proportion for plain UHPC and NanoUHPC

Mix Designation	Raw Materials (kg/m^3)					
	OPC	Nano clay	Aggregate	Sand	Water	SP
Plain UHPC	800	-	433	800	160	11.52
NanoUHPC1	797	3	433	800	160	6.70
NanoUHPC3	776	24	433	800	160	6.98
NanoUHPC5	760	40	433	800	160	7.60

2.2 Procedures

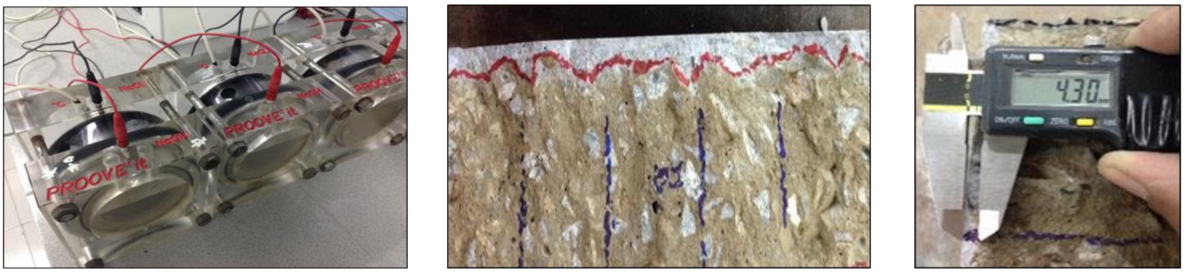
After mixing the concrete, the fresh concrete was poured in square steel mould with size of 100 mm x 100 mm x 100 mm. The concrete cube was casted to determine its compressive strength. Meanwhile, the concrete cylinder specimen was prepared by pouring down the fresh concrete into steel mould with dimension of 100 mm in diameter and 250 mm in height. The concrete cylindrical specimens were prepared for rapid chloride permeability test (RCPT) and chloride penetration depth. All specimens were demoulded at 24 hours and cured in water for 28, 56, 91, 182 and 365 days before the tests conducted. The RCPT procedures are conformed to ASTM C1202 specifications. The RCPT was performed for determining the resistance of concrete to chloride ion penetration. The RCPT setup using *PROOVE' it* instruments. The samples were placed in the test device where the left-hand side (cathode) of the test cell was filled with 3% sodium chloride (NaCl) solution. The anode (right-hand side) of the cell box was filled with 0.3N sodium hydroxide (NaOH) solution. A current input analogue-to-digital converter (A.D.C.) external voltage of 60-Volts was applied to concrete sample of 100 mm diameter and 50 mm thickness. During the test, the main parameter measured was the current flow through the concrete samples for a period of 6 hours. A data logger system recorded the temperature, charge passed and current for every 5 minutes.

At the end of testing, all the concrete samples were removed from the cell and the quantity of coulombs passed through the samples were recorded. Afterwards, the sample was prepared by splitting the sample axially into two (2) sections by using compression machine. Then, 0.1N silver nitrate (AgNO3) solution was sprayed on the splitted surface. Subsequently after the sprayed surface was completely dried, approximately after 30 minutes, white silver chloride precipitation on the surface was visible. It is the effect of chemical reaction of $AgNO_3$ solution that changed the colour of the surface which the part contains chloride to whitish colour. This method called as colorimetric method adopted from Colleparde et al. (1970). In order to obtain the profile of the chloride precipitation, the line along the cross-section of splitted concrete surface that contain chloride was drawn. The stages of RCPT and colourimetric method is shown in Figure 1. The depth of chloride penetration into the sample was measured using digital caliper with minimum of five (5) different location across of the sample and the average readings were calculated. At the end of the RCPT and the chloride penetration depth, the chloride diffusion coefficient was calculated by using Equation 1.

$$D = \frac{0.0239(273+T)L}{(V-2)t}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{V-2}}\right) \tag{1}$$

Where,

D = Non-steady-state diffusion coefficient (x10^{-12} m/s)
V = Applied voltage (V)
T = Average value of initial and final temperature in the anolyte solution (˚C)
L = Thickness of the sample (mm)
x_d = Average value of penetration depth (mm)
t = Time (hrs)



(a) RCPT set up

(b) Whitish chloride front migrating into NanoUHPC

(c) Chloride depth measurement

Figure 1. RCPT arrangement and chloride depth measurement for chloride diffusion

3. Results and Discussion

3.1. Compressive Strength

Figure 2 demonstrates the compressive strength of plain UHPC and a series of nanoUHPC corresponding to age. It noted that the strength of entire concrete increases with curing age increase. UHPC contained 1% nano metaclay develop the strength after 28 days of curing as compared to those of plain UHPC and nanoUHPC containing 3% and 5% of nano metaclay. The strength of nanoUHPC1 develops gradually and the strength significantly increased with prolonged the curing age. As the amount of nano metaclay increased, the reduction of strength was recorded for UHPC incorporated 3% and 5% of nano metaclay. The highest compressive strength obtained at 365 days of age was by nanoUHPC1 recorded 134.79 MPa. It is also found that nanoUHPC1 yielded higher strength up to 10% than those of UHPC specimens. It is noted that the hydration process is slow due to low heat of hydration when the percentage of nano metaclay increased thus slow down the strength gain [21-23]. This is also revealed by Raki et al. [24] who found that higher content of supplementary cementitious material (SCM) in concrete can drastically slower down the hydration process. Therefore, UHPC1 specimens present excellent properties in term of compressive strength. Prolonged the age of curing has provided the filler action and pozzolanic reaction simultaneously contributed to the compressive strength enhancement [25]. This is because the filler effect from the nano metaclay particles with small amount provide good capabilities and easily refine the microstructures. As well documented previously, the concrete produced with pozzolanic materials causing the mix becomes densified from hydration gel process by smoothing the angular and reducing voids between the hydration gels [26,27].

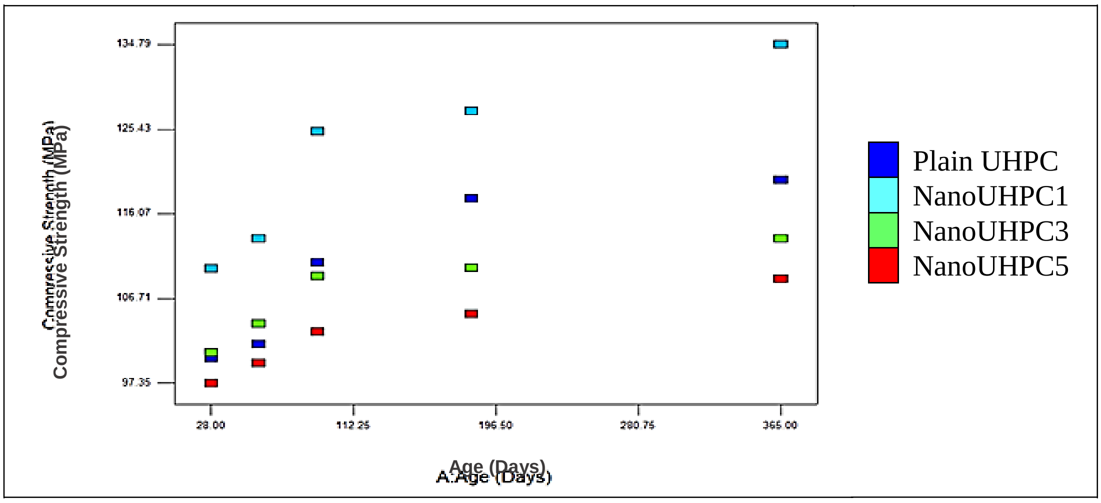


Figure 2. Compressive strength for plain UHPC and a series of nanoUHPC against age

3.2. Chloride Diffusion Coefficient

At the end of the RCPT, the average penetration depth of chloride ions was determined, thus the chloride diffusion coefficient was calculate using Equation 1. Figure 3 displays the chloride ion diffusion coefficient for all series of UHPC. At 28 days of curing, the chloride diffusion coefficient obtained are 1.32 x 10^{-12} m^2/s, 1.11 x 10^{-12} m^2/s, 1.46 x 10^{-12} m^2/s and 1.50 x 10^{-12} m^2/s for plain UHPC, nanoUHPC1, nanoUHPC3 and nanoUHPC5, respectively. Based on the result, it can be stated that inclusion of 3% and 5% of nano metaclay in UHPC did not improve the resistance of chloride ingress corresponding to plain UHPC. It is also noted that the chloride diffusion coefficient for entire concrete specimens decreased with increase the curing age.

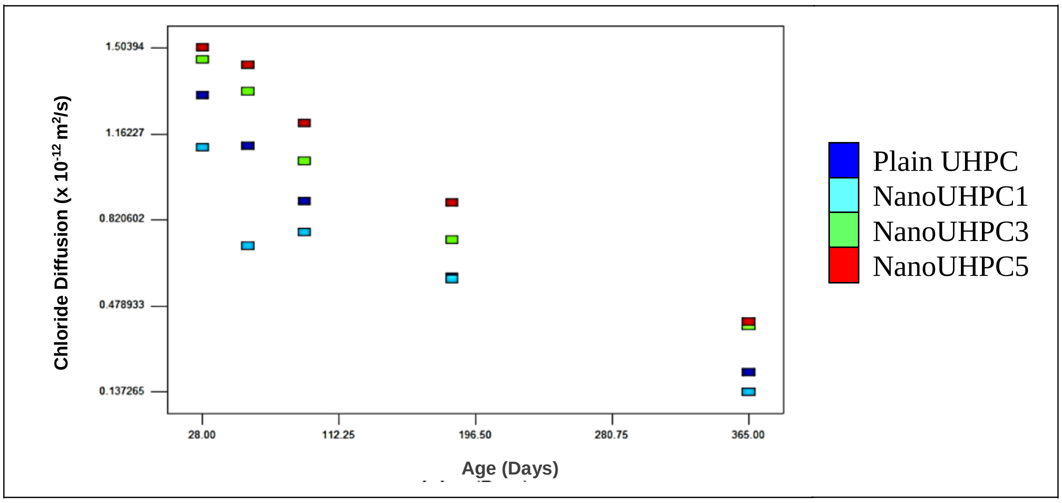
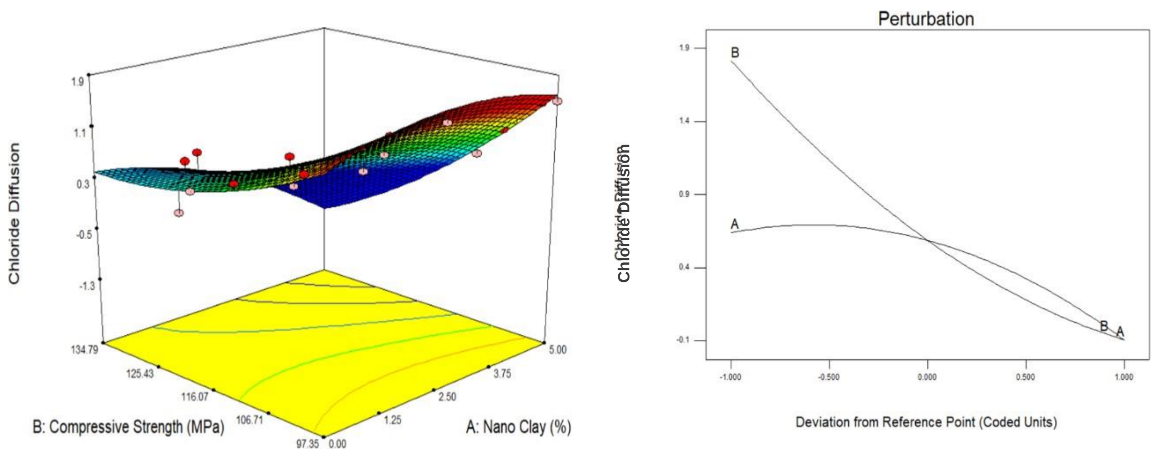


Figure 3. Chloride Diffusion for plain UHPC and a series of nanoUHPC against age

Inclusion of 1% nano metaclay in UHPC improve chloride resistance characteristic thus, lower chloride diffusion coefficient was recorded as well as those of plain UHPC, nanoUHPC3 and nanoUHPC5. At 365 days of curing, it is found that the chloride diffusion coefficient obtained for nanoUHPC1 was 0.14 x 10^{-12} m^2/s and 1.57 times lower than that recorded by plain UHPC. Improved microstructure of C-S-H gel with the presence of 1% nano metaclay is the reason of this phenomenon. The chloride diffusion results are in good agreement with the compressive strength. Tafraoui et al. [14] study revealed that the chloride diffusion coefficient for UHPC with silica fume is lower in chloride penetration. They found that silica fume in concrete can fill the micro-pores between C-S-H paste and pozzolanic material. As pozzolan reaction continues, the strength of concrete increased thus reduce the chloride diffusion rate for the concrete. Several researchers were also reported that inclusion of zeolite and by using low water to cement ratio (w/c) in high performance concrete caused a decrease in chloride diffusion due to the improvement of microstructure [28,29].

3.3. Relationship Between Compressive Strength and Chloride Diffusion Coefficient

The model of response plots to verify the relationship between nano metaclay content and compressive strength towards chloride diffusion coefficient of UHPC is demonstrated in Figure 4. The RSM analysis indicates that the quadratic relationship between content of nano metaclay and compressive strength with respect to chloride diffusion is strong, where the regression coefficient (R- square) was found to be 0.8480. This means that the relationship between nano metaclay content and compressive strength with respect to chloride diffusion is strong about 84.80%. The 3D surface of response plots as in Figure 4(a) used for evaluated the effects of nano metaclay content and compressive strength against chloride diffusion indicating the content of nano metaclay decrease, the chloride diffusion coefficient values also decreased. While, when the compressive strength increased, the chloride diffusion values decreased. This statement confirmed by the perturbation plots as shown in Figure 4(b). A steep slope or curvature in a Curve A shows that content of nano metaclay in UHPC is more sensitive to that compressive strength. It indicating that nano metaclay content has a great influence on compressive strength and chloride diffusion. Therefore, it is believed that lower content of nano metaclay exhibits higher compressive strength resulted lower permeability and slowing the chloride penetration into concrete.



(a) (b)

Figure 4. 3D response surface plots for chloride diffusion coefficient

4. Conclusions

Based on the findings obtained from the study, the conclusions that may be derived from the present study are as follows:

- **a.** It was found that the inclusion of 1% nano metaclay in UHPC is sufficient amount to boost the compressive strength up to 10% compared to plain UHPC.
- **b.** The inclusion of nano metaclay enhances the chloride penetration resistance of UHPC and it was discovered that the use of 1% nano metaclay in UHPC marked superior chloride diffusion.

c. The result on regression analysis obtained the R-square is 0.8480 and significantly strong. It was found that when the content of nano metaclay decreased, the chloride diffusion coefficient also decreases but the compressive strength increased.

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