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Strength and Chloride Content of Nanoclayed Ultra-High Performance Concrete

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Abstract

The major cause for degradation of reinforced concrete due to chloride penetration has been the great research effort. A large number of published literatures on chloride penetration for ultra-high performance concrete have been reported. In this paper, the strength and the chloride resistance characteristic of the nanoclayed ultra-high performance concrete (UHPC-NC) were investigated. Series of ultra-high performance concrete specimens comprise of 0%, 1%, 3% and 5% of nanoclay replacing the total weight of cement were produced. Four (4) series of UHPC-NC specimens were designated as UHPC, UHPC-NC1, UHPC-NC3 and UHPC-NC5 respectively. The workability of fresh UHPC and UHPC-NCs, strength performance and chloride content of UHPC and UHPC-NCs measured using Mercuric Thiocyanate method were investigated. It is reported that all the UHPC mixes have high workability however; UHPC-NC5 recorded the lowest slump reading. It also clearly emerges that replacing 1% of cement with nanoclay enhance significantly the compressive and splitting tensile strength as compared to that without nanoclay. The optimum nanoclay replacement level was found to be 1% from the total weight of OPC for strength, but not for chloride diffusion. In term of total chloride content, it is revealed that the incorporation of nanoclay into UHPC mix leads to the reduction of chloride diffusion of the resulted UHPC. It shows that 5% replacement level of nanoclay effectively decreases the chloride diffusivity in UHPC.

Keyword: *nanoclayed ultra-high performance concrete; nanoclay; workability; compressive strength; splitting tensile strength; chloride content*

1. Introduction

Concrete is widely used in construction industry and Portland cement most commonly used as construction material. Commonly, concrete is an excellent protection for steel reinforcement but exposure to various environmental conditions during its service life may accelerate the destruction process (Roa-Rodriguez *et al.*, 2013). Several researchers claimed that the presence of chloride in reinforced concrete can lead to corrosion of the reinforcement by destroying the passive layer on the steel surface (Mustafa & Yusof, 1994; Yeih *et al.*, 1994; Bai *et al.*, 2003; Maes & De Belie, 2014). Nowadays, the amount of chloride that can penetrate into hardened concrete is a major cause for pitting corrosion in concrete structures. The amount of chloride in concrete that cause destruction of steel passive layer generally referred as critical chloride content. Therefore, the problem of corrosion of steel in concrete is very important (Leng *et al.*, 2000). Several researchers also found that the causes of steel corrosion are not only due to chloride penetration. There are many factors govern the phenomenon of chloride penetration into concrete such as the type of cementitious material, the water-cement ratio, curing time, period of exposure to chlorides and other physical factors (Castro *et al*., 2001; Win *et al*., 2004; Huiguang *et al*., 2011 and Roa-Rodriguez *et al*., 2013).

Regards to this, Samy and Ji (1999) indicated that utilization of high performance concrete (HPC) which has high strength and durable are recommended to solve the chloride diffusion problem in normal concrete. They found that HPC with the replacement of cement by zeolite, pulverized fuel ash and silica fume at levels from 5% to 30% would increase the strength and improvement the chloride diffusion characteristic. HPC with fly ash and blast furnace slag also resulted in the good resistance to chloride diffusion (Leng *et al*., 2000). Gastaldini *et al*., (2010) reported that increase in the rice husk ash contain would reduce the chloride ingress in concrete. Previous researchers also reported that addition of fly ash; blast furnace slag and silica fume can reduce the pore size of concrete, as a result concrete become denser hence, increase the concrete strength and decrease the chloride diffusivity (Tikalsky *et al*., 1986; Page *et al*., 1986 and Maslehuddin *et al*., 1989). The achievement of such high strength concrete has been possibly through the introduction of pozzolanic materials as a cement replacement.

A study conducted by Bai *et al*. (2003) on HPC produced from Portland cement blends with pulverized fuel ash and/or metakaolin shows a significant beneficial effect of the latter on chloride penetration and penetration depth of the resulted concrete. It was recognized that concrete containing metakaolin improved in strength at early age and the improvement was obvious as curing time was prolonged up to 18 months. Also, Boddy *et al*. (2001) revealed that concrete containing highest high-reactivity metakolin content would decrease the chloride permeability and increase resistivity. It was found that the strength of the concrete increased with increasing content of high-reactivity metakolin. On the other hand, it was found that 8% level of silica fume replacement in HPC would slow down the amount of chloride penetrate into concrete. This is due to high fineness of the silica fume and more discontinuous pore structure is produced in concrete (Hong and Hooton, 2000). The use of 5% to 10% silica fume as a binder has a very positive effect on reducing the chloride ingress in concrete (Sandberg *et al*., 1998). However, no benefit was found for concrete with fly ash. Madani *et al*. (2014) also revealed that the use of nanosilica concrete enhance the chloride permeability characteristic at early age of the concrete. The use of slag on chloride penetration resistance of concrete also increases with increasing slag replacement level that found by Otieno *et al*. (2014).

Up to date, the existing of advanced technology of ultra-high performance concrete (UHPC) has boosted up the usage of concrete in construction industry. UHPC is one of the most advanced concrete which is has better characteristic in terms of high strength and superior durability as compared to normal concrete. UHPC can be defined when the compressive strength can achieve more than 150 MPa (Richard & Cheyrezy, 1995; Graybeal & Tanesi, 2007; Sorelli *et al*., 2008). In addition, UHPC has high bending strength, resistance to deicing salt attack, very strong, durable and ductile. The problem with UHPC is the production requires special ingredients and high cementitious materials which is usually using silica fume (Cherezy, 1995 and Matte, 1999). As known, silica fume is costly and require advanced technology to produce it. Therefore, the use of nano-material is one of the oppor the use of cement. In this present study, to cater the measures for chloride content in UHPC incorporating nano-material namely nanoclay was studied. Besides, the effect of nanoclay as cement replacement in UHPC due to chloride diffusion is still not adequately covered and has not been established so far. Therefore, it is proved that concrete incorporating cementitious content as a part of conventional cement affect the chloride penetration to transport in. The effect of using different levels of nanoclay as cement replacement was evaluated with respect to workability, strength and chloride content.

2. Experimental Programme

2.1 Materials

In this study, four (4) series of nanoclayed UHPC were cast. An ordinary Portland cement (OPC) Type I provided by local supplier was used as a binder. The properties of OPC are equivalent to BS EN 197-1: 2000 specification. The control concrete mix (UHPC) was prepared using OPC while the nanoclayed UHPC mixes incorporating nanoclay were prepared by replacing the OPC partly with different levels of nanoclay which are 1%, 3% and 5% from the total weight of OPC used. The crushed gravel was used as the coarse aggregate with a nominal size of 20 mm. Meanwhile, fine aggregate passing 5 mm was used as sand.

In order to obtain a desired workability of UHPC and nanoclayed UHPC, the hyper-superplasticizer namely Glenium ACE 389 SURETEC supplied by BASF (M) Sdn. Bhd. was used. The dosage of hyper-superplasticizer used are various from 0.84% to 1.44% depending on the amount of nanoclay content incorporating into the mixes. In this present research, the raw nanoclay powder supplied by Sigma Aldrich (M) Sdn. Bhd. was used to produce the nanoclayed ultra high performance concrete. The calcination process of raw nanoclay was performed by heating the raw nanoclay using high temperature furnace carbolite at the temperature of 700°C for 3 hours. This process was carried out in order to produce the chemically reactive to form the amorphous from crystalline structure. Field Emission Scanning Electron Microscopy (FESEM) analysis was carried out to verify the chemical compositions of OPC and nanoclay powder. Table 2.1 shows the chemical composition of OPC and nanoclay after calcination process.

Table 2.1: Chemical composition of ordinary Portland cement and nanoclay (wt%)

% Oxide	Ordinary Portland Cement	Nanoclay
SiO_2	11.6	65.9
Al_2O_3	2.2	15.1
CaO	75.17	4.3
TiO_2	0.4	0.9
Fe_2O_3	5.38	11.4
K_2O	0.43	0.24

2.2 Mix Designation and Specimen Fabrication

Four (4) series mix proportion of ultra-high performance concrete and nanoclayed ultra-high performance concrete were prepared. The ultra-high performance concrete mix was designated as UHPC or control mix (0% nano clay). Consequently, the UHPC mixes that contained different levels of nanoclay which are 1%, 3% and 5% were designated as UHPC-NC1, UHPC-NC3 and UHPC-NC5 respectively. The mix proportion of the UHPC and UHPC-NCs are tabulated in Table 2.2. The water to cement ratio used was constant at 0.20.

Table 2.2 Mix proportion of UHPC and UHPC-NCs

Mix Design	Raw Materials (kg/m^3)					
	Cement	NC	Agg.	Sand	Water	Glenium
UHPC	800	0	433	800	160	16
UHPC-NC1	797	8	433	800	160	16
UHPC-NC3	776	24	433	800	160	16
UHPC-NC5	760	40	433	800	160	16

In order to determine the strength properties of UHPC and UHPC-NCs specimens, the cube specimens with dimension of 100 mm x 100 mm x 100 mm were produced for compressive strength test. Also, cylinder specimens with 100 mm diameter and 200 mm height were cast to determine the tensile strength and chloride depth. The cast specimens were demoulded after 24 hours casting. All the specimens were cured in water for 7, 28, 56 and 91-days before subjected to compressive and tensile strength test. However, to determine the chloride content, specimens were taken out from the water after 7 days of immersing in 3% sodium chloride (NaCl) solution. The samples were sealed at the top and bottom using waterproofing membrane. This is because to prevent the ingress of chloride at the top and bottom of specimens before immersion.

2.3 Testing Procedures

In this study, the testing method can be divided to three (3) comprises of workability of fresh concrete, strength properties and chloride content of UHPC and UHPC-NCs specimens. The strength performance namely compressive strength and tensile strength were conducted. For chloride content, the amount of chloride penetrating UHPC and UHPC-NCs specimens were determined. The following sub-sections explain each test.

2.3.1 Workability

The workability of fresh UHPC and UHPC-NCs was performed as accordance with EN 12350-2:2009. The targeted slump is between 160 mm to 180 mm. The slump of fresh UHPC and UHPC-NCs are tabulated in Table 3.1. The slump was measured with indication of high workability concrete if the slump is more than 160 mm.

Table 3.1: Consistency of fresh UHPC and UHPC-NC concrete

Mix Designation	Slump Reading (mm)	Indication
UHPC	178	High
UHPC-NC1	171	High
UHPC-NC3	167	High
UHPC-NC5	163	High

2.3.2 Compressive Strength and Tensile Strength Test

In order to determine the strength development of UHPC and UHPC-NCs specimens, the compressive strength and tensile strength test were performed. The tests were conducted after 7, 28, 56 and 91-days cured in water. Compressive strength was determined in accordance with BS EN 12390-3:2009 and tensile strength test follows BS EN 12390-6:2009. The tests were carried out to determine the optimum percentage of nanoclay incorporated in UHPC mix as a cement replacement material.

2.3.3 Chloride Content Test

To examine the influence of nanoclay as a cement replacement in UHPC, the chloride content was investigated. All the UHPC and UHPC-NCs specimen were immersed in 3% NaCl solution. The exposure tooks for 7, 28, 56 and 91-days before the chloride content and the penetration were measure. After the exposure, the specimens were taken out from the NaCl solution. The specimens were washed using tap water and left in temperature room for 1±0.5 hours. Then, the chloride content for each immersed specimen was measured.

For chloride content determination, the specimens were drilled horizontally for different depths of 10, 20, 30, 40 and 50 mm from the concrete surface (BS 1881-124:1988). Purpose of this drilling is to obtain the powder in concrete. Afterwards, 1g±0.1g of concrete powder for each depth was weighed and mixed with 10 ml of deionized water. The mixture was stirred continuously for 30 minutes using shaker. Next, 5 ml nitric acid was added to the mixture and stirred again for 30 minutes. After the mixture was homogenously mixed, the mixture was filtered using filter paper until filtered off. Accordingly, the filtered mixture was prepared for chloride content test using HACH spectrometer. The test preparation follows Mercuric Thiocyanate method (Method 8113).

3. Results and Discussion

3.1 Workability

The findings for workability for fresh UHPC and UHPC-NC concretes were tabulated in Table 3.1 earlier. The replacement of nanoclay reduces the slump readings of UHPC-NC mixes. UHPC-NC5 mixes which contains of 5% nanoclay records the lowest slump reading. The higher of content of nanoclay as a cementitious material, the greater affecting in water demand. This is because the influence of larger surface area of nanoclay as compared to OPC creates more spaces in the paste. Thus, nanoclay paste needs more water to maintain the level of consistency. It is also shown that all the four (4) UHPC mixes can be categorized as high workability mixes as according to EN 12350-2:2009.

3.2 Strength Performance

Generally, the use of nanoclay in UHPC as a cement replacement material can improve the compressive strength of UHPC-NCs with respect to increase of curing days. Results on compressive strength of the UHPC and UHPC-NC series are displayed in Figure 3.2. At early stage, it is found that incorporation of nanoclay does not show positive effect to the strength. On the other hand, at 90-

UHPC-NC specimens obtained highest compressive strength as compared to that UHPC itself. The highest compressive strength was recorded from UHPC-NC1 specimen.

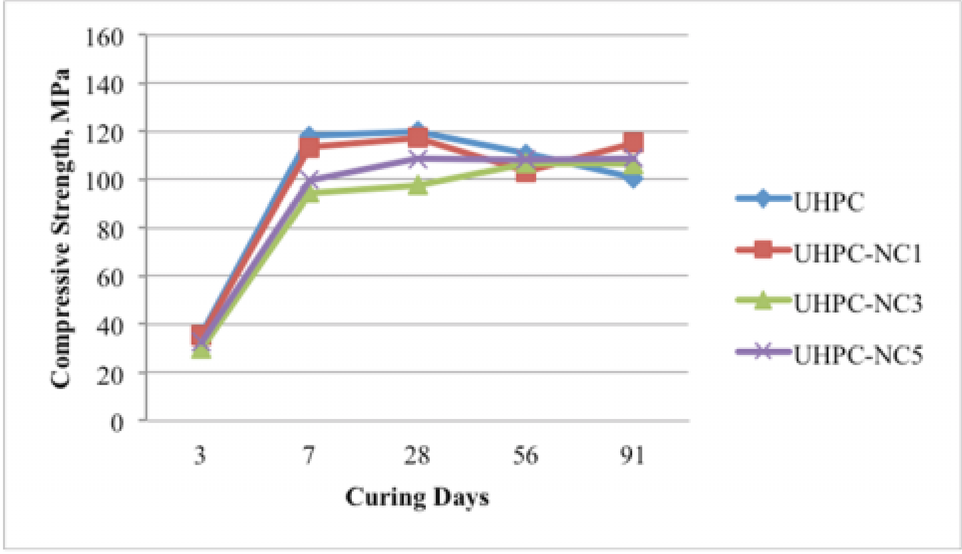

Figure 3.2: Compressive strength of UHPC and UHPC-NC specimens

For splitting tensile strength, the results recorded are graphically illustrated in Figure 3.3. It is noted that the control specimen namely UHPC without replacement of nanoclay attained highest splitting tensile strength as compared to those UHPC-NC mixes. However, the tensile strength of UHPC-NC1 increase significantly about 8.92% when compare to UHPC itself. Therefore, UHPC-NC1 with replacing 1% nanoclay obtained highest tensile strength.

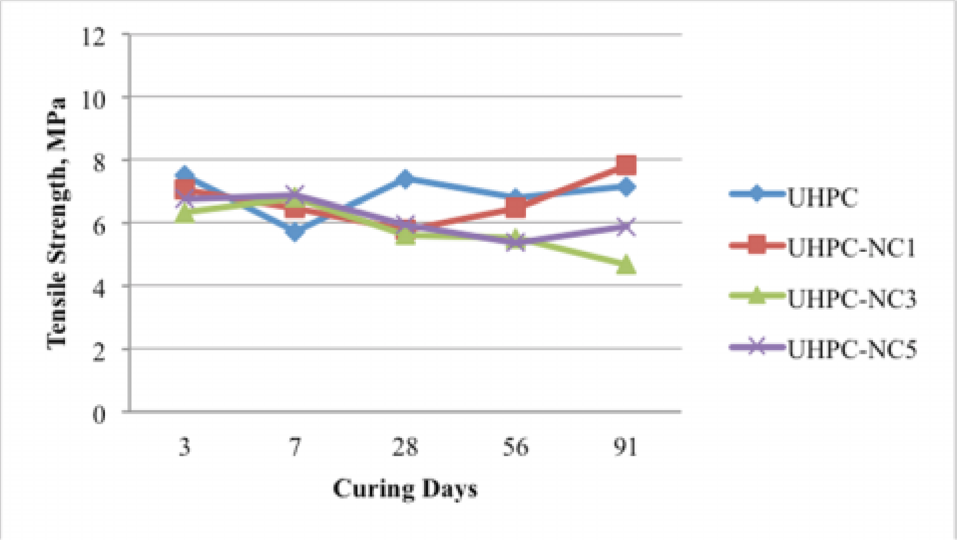

Figure 3.3: Tensile strength of UHPC and UHPC-NC specimens

It is clearly shown that the nanoclay used in producing UHPC-NCs are dominant in prescribing the increase in compressive strength and splitting tensile strength. It also shows that nano particles of nanoclay influence the strength enhancement. This finding agreed by Morsy *et al.,* (2010) also reported that nano particles enhanced strength by physical filler effect of nano particles in spaces of hardened structure of UHPC. Overall, UHPC with 1% nanoclay (UHPC-NC1) shows the optimum replacement in total cement. The strength development of UHPC-NC1 is cause by a proper dilution effect and resulting in a uniform and homogenous micro-structure of concrete. Furthermore nanoclay acts as ultra-filler by replacing and filling the micro voids also supports the phenomena. As well-documented in Zhang *et al.,* (2007) who indicated that compressive strength of concrete increased with little amount of nano-silica in the concrete when compare to concrete without nano-silica. Li & Chen (2012) also verified that filling effect of nanoclay up to 1% of replacement in OPC has made the UHPC much stronger in tensile strength.

3.3 Chloride Content

The results highlighted the influence of the nanoclay as a cement replacement in producing the UHPC. The chloride content with respect to cover depth for UHPC and UHPC-NCs specimens exposed to 3% NaCl solution were graphically presented in Figures 3.4 to 3.7, for nanoclay replacement levels 0%, 1%, 3% and 5% respectively. The chloride content analysis was conducted for UHPC and UHPC-NC specimens at 3, 7, 28, 56 and 91-days of age. It is found that the chloride content generally increased with the time of exposure and decreased as it goes deeper inside the specimens.

The chloride diffusion value shows that the UHPC incorporating 5% nanoclay has been marginally improved the chloride resistance as compare to UHPC, UHPC-NC1 and UHPC-NC3. The UHPC-NC5 has found 0.64 to 1.63 times more resistant towards the chloride penetration with respect to expose days as compare to UHPC specimens. The results indicate that by replacing 5% OPC with nanoclay in UHPC further increases the chloride penetration resistance to that of respective grade of control concretes.

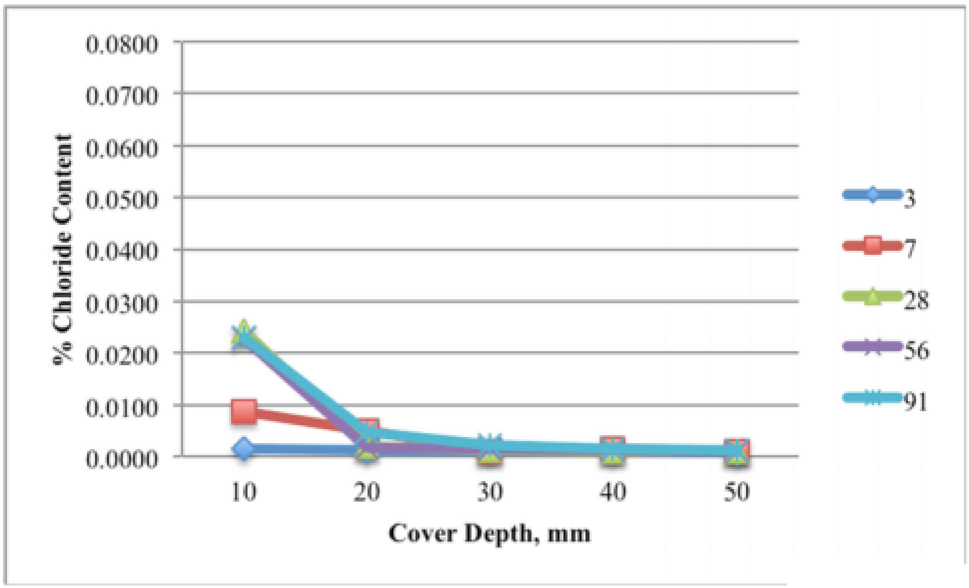

Figure 3.4: Chloride content of UHPC specimens

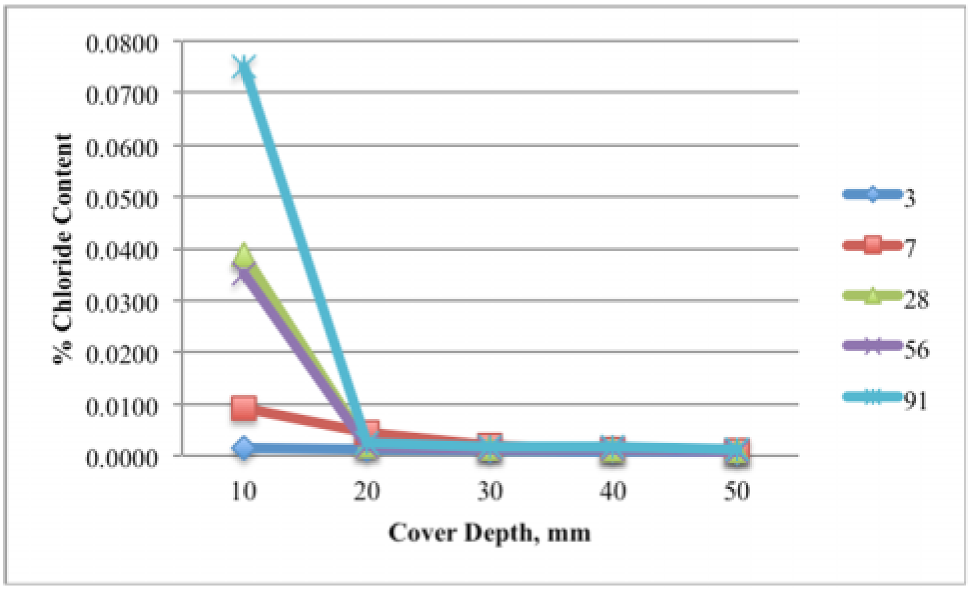

Figure 3.5: Chloride content of UHPC-NC1 specimens

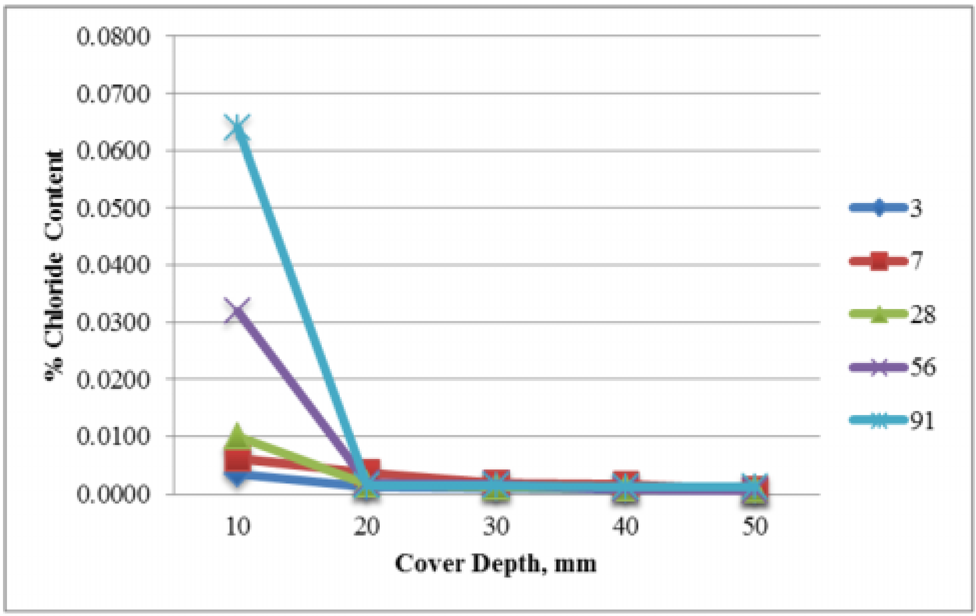

Figure 3.6: Chloride content of UHPC-NC3 specimens

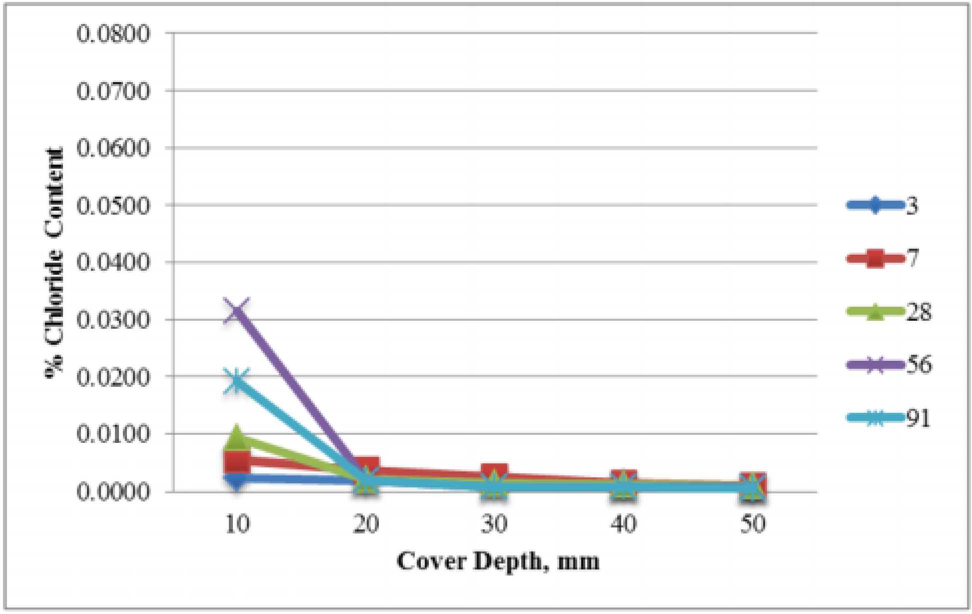

Figure 3.7: Chloride content of UHPC-NC5 specimens

It is revealed that as the nanoclay level increases, there is a very marked reduction in the chloride content particularly within the first 10 mm depth of concrete. Also, the incorporating 5% nanoclay in UHPC increases the chloride resistance. Bai *et al*. (2003) also found that the chloride penetration content reduce in concrete when the concrete made of pulverized fuel ash and metakoalin as a cement replacement.

It has been observed that when the age of UHPC specimens is prolonged, the chloride content in the outer region for UHPC made with 5% nanoclay. Well documented in Bai *et al*. (2003) verified that concrete containing high replacement of pulverized fuel ash and metakoalin particularly would limit the penetration of chloride due to pozzolanic reaction with increase in curing time. From the present result, it is clearly publicized that UHPC-NC5 produces finer pore structure due to the formation of the pozzolanic reaction within the capillary pore spaces. The pore system will also become finer and more segmented with increase in exposure time due to continuing pozzolanic reaction. It has proved by Hong & Hooton (2000) who claimed that the use of silica fume in producing concrete due to finer particles and more discontinuous pore structure. Thus, the chlorides will ingress slowly in concrete. The used of nano-silica in concrete will delay and reduce chloride penetration (Madani *et al*., 2014)

4. Conclusions

From the findings, the conclusions can be drawn as follows:

1. Incorporating nano clay for different level of replacement alters the water demand to maintain the workability. It is demonstrated that increase in nanoclay content decrease the workability.
2. It is indicated that the contribution of nanoclay to compressive and tensile strength are obvious at later age. It also revealed that 1% nanoclay is the optimum content.
3. Significant reductions in chloride penetration content occur when the cement

content in UHPC is partially replaced with nanoclay. Nanoclay changes the chloride binding capacity with age exhibited. It shows that 5% nanoclay is effective in decreasing the chloride transport in UHPC.

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