Investigating the Impact of Nano-Calcined Halloysite on Concrete Durability under Chloride Attack

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Abstract

The impact of aggressive agents, especially chlorides, on concrete structures is a significant challenge in the field of engineering. The presence of chlorides leads to corrosion and deterioration of concrete, affecting its performance. Chlorides penetrate the concrete, leading to the destruction of the protective layer around the reinforcing steel, which results in the corrosion of the steel and the formation of rust. This corrosion negatively affects the bond strength between the steel and the concrete and can also cause cracks on the concrete surface, reducing its durability. To address this challenge, a research study was conducted to explore the use of nanomaterials, specifically nano-calcined halloysite, to improve the performance and durability of concrete. The aim was to investigate the impact of incorporating halloysite in concrete on the penetration of chlorides and the subsequent corrosion of reinforcing steel rebars.

Three different concrete mixtures containing varying percentages of halloysite (1.5%, 3%, and 4.5%) were examined. The researchers evaluated the water absorption rates and migration coefficients of these mixtures. Additionally, the impressed current technique was utilized, where a 14mA current was applied for 26 days to accelerate the corrosion of steel rebars. The results of the study demonstrated the effectiveness of incorporating halloysite in concrete to enhance its properties. The mixture containing 3% and 4.5% of halloysite (CHNC) achieved the desired objectives, significantly reducing water absorption. For example, the mixture with 4.5% CHNC showed a 42.99% reduction in water absorption after 7 days. This decrease in water absorption also led to a considerable decrease in the migration coefficient of chlorides and their penetration in the concrete. Furthermore, the inclusion of 4.5% halloysite and 25% ground granulated blast furnace slag (GGBS) in the mixture further improved its performance.

Keyword: Halloysite- concrete durability -impress current- migration coefficient-nano_clay.

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1.1.Introduction

Concrete withstands many environmental threats that have the ability to deteriorate it and reduce the length of its service life. One of concrete’s most dangerous enemies is chloride ions, which penetrate concrete and affect its durability in two stages according to Tuutti [1]. The first stage (the initiation) involves the penetration of the chloride ion into the concrete, but involves limited damage of the reinforcing steel. The second stage, called the propagation phase, occurs when the continuous penetration of chloride ions comes in contact with the reinforcing steel and causes corrosion. The size of the reinforcing steel then increases as a result of rust, which leads to the formation of cracks and the spalling of the concrete [1]. The microstructure of concrete has inherent properties that transport the external fluid (liquids and gases); chloride ions, therefore, can penetrate the concrete through three mechanisms (diffusion, absorption, and permeability). Chloride ions can occur either externally, through de-icing and exposure to marine environment, or internally, from either contaminated aggregates or mixed and treated water containing chloride ions [2]. This creates an urgent necessity to either eradicate or reduce the effect of this problem; there have been attempts to partially replace cement with supplements cementitious materials (SCMs) such as fly ash, silica fume, and slag. Science is constantly evolving and ideas regarding using natural materials, reducing carbon dioxide emissions and utilizing clay minerals and calcined clay minerals as SCMs continue to become more mainstream. Calcined clay minerals are characterized by being better than minerals in their normal state; when thermally treated, the pozzolanic activity of the material increases. In a study conducted on the effect of adding metakoline on the properties of mortar and concrete offered positive results, showing its ability to increase the resistance of the early and final ages of both mortar and concrete; it also improved permeability reduction and increased the durability of both concrete and mortar [3]. In this research, concrete was produced by partially replaced cement by a natural, non-toxic material from a group of kaolin clays is called halloysite. Halloysite is a tube-hole material containing two layers, a tetrahedral layer of silicon molecule surrounded by 4 oxygen atoms, and an octahedral layer containing an aluminium molecule surrounded by a basic hydroxyl, and it contains water between the two layers [4]. The chemical formula of halloysite is ($Al_2(OH)_4Si_2O_5.nH_2O$); when n = 2, the hydrated form of halloysite is referred to as "halloysite-(10Å," with one layer of water molecules present between the multilayers and the "10Å" designation, indicating the d001-value of the layers. The dehydrated structure of halloysite (when n = 0) is known as "halloysite-(7Å)" and can be obtained by removing the interlayer water molecules in a mild heating and/or vacuum environment [5]. This nano-clay resulting from erosion or hydrolysis of either mother rocks, mica, and feldspar, or volcanic rocks.

It is widely distributed around the world and have been used in many fields, including the agricultural, medical and industrial sectors. In the last a few years researchers were investigated adding the halloysite to cement mortar, Farzadnia [6] found adding 3% of halloysite to cement mortar decreasing its flowability by 65% and increasing its compressive strength by 24%. Additionally, Razzaghian [7] found that, , slump and flowability of cement mortar with 3% of HNTs were reduced by 31% and 29%, respectively; and electrical resistance increased by 28% and the compressive and flexural strength of the mortar improved by up to 25% and 20%, respectively .Previous research has examined the behaviour of cement mortar with halloysite nano clay; however, in this research, the performance of and the characteristics of concrete with halloysite nano clay will be examined in terms of durability, particularly regarding the penetration of chlorides and corrosion, which is one of the most dangerous potential threats to the durability and service life of concrete structures.

2. Experimental Work

2.1. Material

Ordinary Portland cement (OPC) type I, which is manufactured in Iraq under the trade name Al-Mass, was used in this research, and it conforms to the Iraqi specification. Calcined Halloysite Nano Clay (CHNC) was sourced from China for the purpose of this research. It has a chemical formula of $Al_2Si_2O_5(OH)_4.2H_2O$ with a molecule weight of 294.19 g/mol. Ground granulated blast furnace slag (GGBS) was supplied by Hanson cement group, which is UK-based; it has a relative density of 2.90 g/cm2. The chemical composition of the OPC, CHNC, and GGBS are shown in Table 1. Natural fine aggregate with a maximum particle size of 4.75 mm and fineness modulus of 2.41 was employed. The coarse aggregate used in this research is a local natural aggregate from the Al Nabaa region of Iraq; its maximum size is 20 mm. Polycarboxylate superplasticizer (SP) was used in study with percentage of 0.5% and 1%, replacement by mass of cement.

Table 1: Chemical Compositions of OPC Powder, CHNC and GGBS

	CaO	SiO_2	Al_2O_3	K_2O	Fe_2O_3	MgO	Na_2O	TiO_2	SO_3
Cement	60.7	20.52	5.33	-	3.98	2.44	-	-	2.45
halloysite	0.2	45.8	37.3	6	2.5	1.2	1.2	0.7	-
GGBS	41.95	35.59	14.32	-	0.35	7.41	-	0.55	0.09

2.2. Nanoclay Dispersion, Mixture Proportions and Concrete Preparation

To obtain a good concrete mixture and to ensure the full benefit of the CHNC, halloysite material was firstly dispersed with tap water in the mixer for 10 minutes and added to the mixture of concrete that was designed according to the American Standard ACI 211.1, as shown in Table 2. Where the materials were mixed then a plasticizer was added, and then the CHNC slurry and the rest of the mixing water were added. In mixture containing GGBS, it was mixed with cement by dry mixing, and the rest of the mixture components of halloysite, plasticizer, and the rest of the mixing water were added. The number of concrete mixtures was 3, divided into one for a strength of 40 MPa (H1) and the second for 50 MPa (H2), and the last one contains GGBS of 25% by mass of cement (H3). Three percentage of CHNC (1.5, 3 and 4.5%) as well as the reference mixture (CHNC=0) were replaced by mass of cement in the main mixtures (H1, H2 and H3).

Table 2: Mix Proportion of Concrete (Kg/m^3).

Mix	Cement Kg/m^3	CHNC (%)	GGBS Kg/m^3	FA[1] Kg/m^3	CA[2] Kg/m^3	Sp %	w/c
H1	370	0	-	706	1080	0.5	0.5
	364.45	1.5	-				
	358.9	3	-				
	353.35	4.5	-				
H2	420	0	-	678.4	1080	1	0.45
	413.7	1.5	-				
	407.4	3	-				
	401.1	4.5	-				
H3	277.5	0	92.5	706	1080	0.5	0.5
	273.34	1.5	92.5				
	269.175	3	92.5				
	265.013	4.5	92.5				

[1] Fine Aggregate, [2] Coarse Aggregate, CHNC and SP were added as percentage of mass of cement.

2.3. Test of Concrete

2.3.1. Absorption and Porosity

The water absorption test of each cube sample (100*100*100mm) were carried out according to the specification (ASTM C642-13) after 7, 28, and 90 days.

2.3.2. Chloride Migration Coefficient Test

This test was performed according to (NT-Build 492-1999). Three samples of (dia100*thick 50mm) were tested at 28 and 90 days.

2.3.3. Impressed Current for Corrosion

A concrete prism with dimensions of 100*100*200mm was used in this test. Firstly, the 15 cm length steel bar were weighed and embedded in concrete prism with at least 2 cm cover. After 28 days of curing, the samples were placed in a basin containing a stainless-steel grid as the cathode and a container of water contained 5% NaCl, as shown in Figure 1. The steel bars were connected with copper wires including 1kΩ resistors to work as anode then connected with DC power supply. According to Faraday's Law (see Equation 1), to achieve 10% corrosion in a steel bar, the samples must be exposed to impressed current in a chloride solution for 26 days. After that time, the samples were split, and the steel bars removed in order to measure the corrosion percentage by computing the difference in weight of steel bar before and after the exposure. The two parts of the split concrete were used to measure the amount of chloride penetration; they were sprayed with 0.1 M of $AgNO_3$ solution [8].

$$t = \frac{m * z * f}{M * I} \dots\dots\dots\dots (1)$$

Where:

T=time (second); M=mass loss due to corrosion (gm); Z=valance (2); F=Faradays constant (96480 A.sec); M=atomic weight of metal (55.85) and I=Imposed current (A).

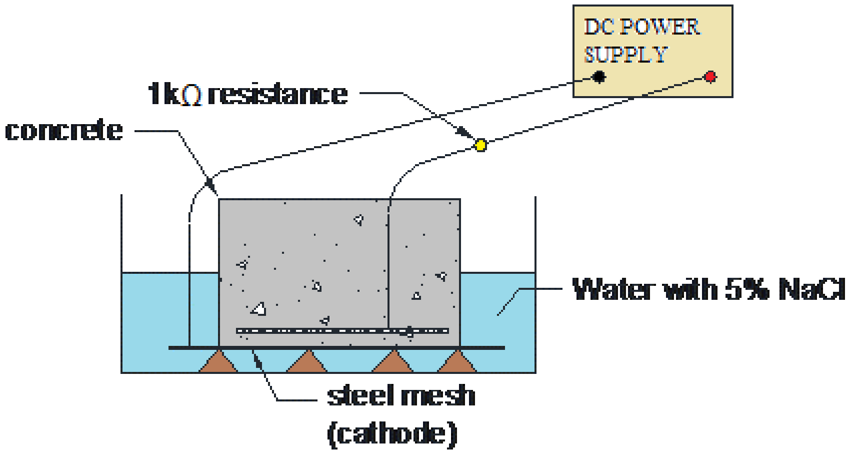

Figure. 1: Sketch for Impress Current test

3. Results and Discussions

3.1. Water Absorption and Porosity

The results of total water absorption of concrete for each of the mixtures H1, H2 and H3 for different percentage of CHNC at 7,28 and 90 days are presented in Figure 2. The results showed that the replacement of calcine halloysite with cement reduced the water absorption, as there was a decrease in the results of the mixture H1 samples for the three percentage. The ratio 1.5% had a slight decrease in water absorption by - (0.54, 1.67 and 2.81%), however there was a clear decrease in the water absorption of concrete samples having 3 and 4.5 % of the CHNC compared with the control mixture by – (25.20, 24.44 and25 %) for samples with CHNC 3 % and (28.46, 28.89 and 31.74) for samples with CHNC 4.5% at 7,28,90 days respectively. This reduction in water absorption is an indication of the improvement of the porous structure of concrete containing CHNC with high proportions. As for the H3 mixture, there was a decrease in the reference mixture containing GGBS with the H1 reference mixture by about - (14.63, 13.61and 15.17%), and this is due to the pozzolanic activity of GGBS, which works to improve the binding properties of the matrix and reduce the water absorption, also pore refinement and the formation of discontinuous pores in concrete [9]. Also, CHNC has a considerable role when adding it with the GGBS, as both the ratio of 3 and 4.5 % worked to reduce the amount of water absorption – (18.41, 17.36 and 16.32%) for 3% CHNC and - (32.70, 31.38 and 35.43%) for 4.5% of CHNC at 7, 28 and 90 days this due to the nanoscale size of halloysite, they can penetrate into small spaces between cement particles and fill voids, leading to a more compact structure with fewer pores. The combined effect of Halloysite nanoparticles and GGBS can significantly enhance the properties of concrete structures and reduce their water absorption. Halloysite nanoparticles can fill voids and improve the packing density of the concrete, while GGBS can increase the amount of C-S-H gel and reduce the porosity of the cementitious material. This can lead to a denser and more durable concrete structure with lower water absorption. As for the H2 mixture, it was noticed that it has less absorbency because it has a high-strength concrete with less w/c compared with other mixtures. And the addition of CHNC has an additional and clear improvement in reduce the water absorption of concrete for both the ratio of 3 and 4.5% due to the decrease in interconnected voids and provide a dense matrix and the reduction was 39.88, 36.86 and 36.04 for 3% CHNC and 42.99, 33.01 and 29.55% for 4.5% at 7, 28, 90 days respectively.

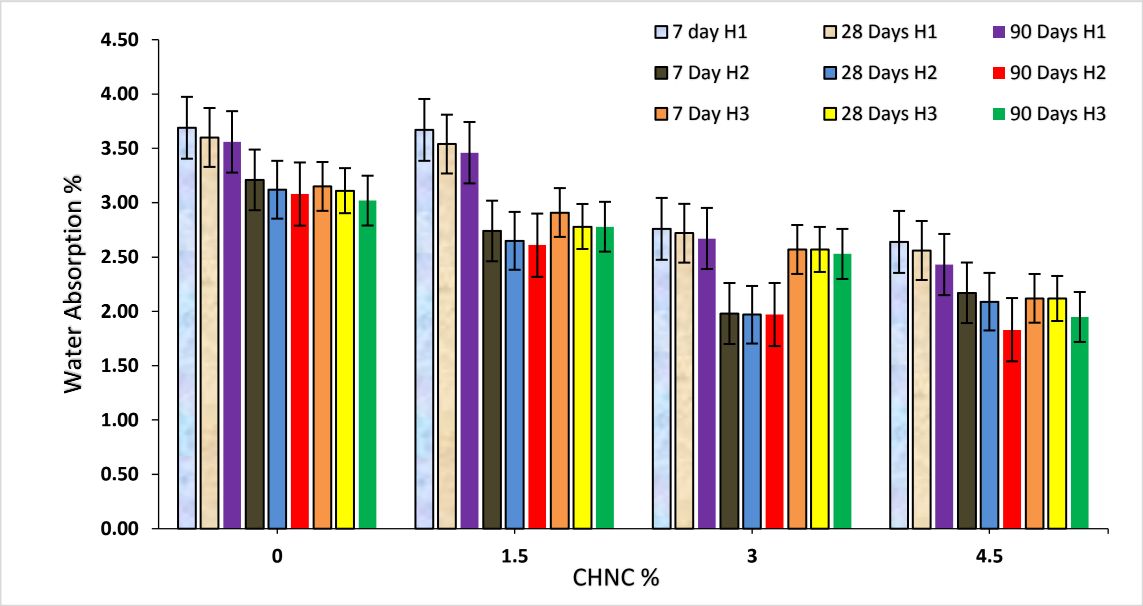

Figure.2: Water Absorption Result with CHNC Replacement

3.3. Chloride Migration Coefficient (D_{nssm})

In Figure 3, the results of the chloride migration coefficient test at 28 and 90 days are illustrated. It is worth noting that the values of the migration of chloride depth at 90 days were less than the values at 28 days for all mixtures when the different percentages of CHNC replacement were increased as shown in Figure 4. There was a clear decrease in D_{nssm} in mixture H2, which is classified on high strength concrete; this decrease was 15% less than the control mixture at 28 days and this is because nanomaterials have a great filling ability due to their small size, and can fill the pores by generating a gel [10]. The reduction in D_{nssm} for H3 mixture was 9.31% as compared to the reference mixture at 28 days in H1. This was due to the size of the GGBS granules; they are smaller than the cement particle. As such, according to the micro-filling characteristic of GGBS, they fill the voids in the microstructure of the cementitious paste and bind with the aggregate, making the concrete more compact and reducing the ability of aggressive materials to penetrate it [11]. This effect is clear in the results of the absorption test, which showed a clear decrease of 15.17% in the mixture containing GGBS at 90 days as compared with the control mixture .

Halloysite significantly reduced the migration coefficient as the replacement percentage increased. The results showed that the lowest diffusion coefficient was at the replacement of CHNC 4.5%. the D_{nssm} for H1 decreased by 21.21% at 90 days compared to 28 days, and by 45.30% and 54.18% for H2 and H3 respectively. This indicates that concrete containing halloysite is more resistant to chloride penetration.

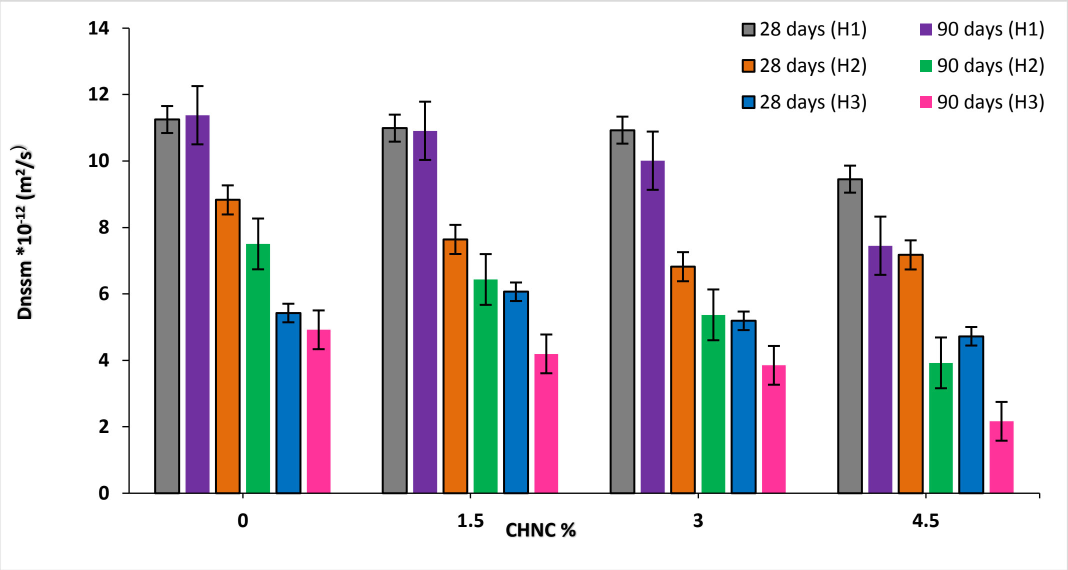

Figure.3: Chloride Migration Depth with CHNC Percentage at 28 and 90 Days

The penetration of chloride ions primarily depends on the permeability and the microstructure of the concrete, and CHNC clearly reduces the permeability due to the decrease in the capillary pores of the concrete as a result of the continuation of the hydration process; the CHNC reacts with calcium hydroxide to form additional gel products that fill the pores, making the concrete is less permeable.

Figure 4: Chloride Migration Depth at A: 28 and B: 90 Days

3.4. Depth Penetration of Chlorides in Impress Current Test

The impressed current test is an accelerated simulation of the corrosion process of reinforcing steel; it is an electrochemical process that determines the ability of halloysite to reduce the corrosion of a steel bar embedded in a concrete mixture. The penetration of chlorides into concrete is one of the primary causes of corrosion. However, result has shown that the incorporation of CHNC into concrete can reduce the amount of chloride penetration. Specifically, it has been observed that the amount of chloride penetration into concrete containing CHNC with concentrations of 1.5%, 3%, and 4.5% is lower compared to concrete without halloysite. It was found that the depth of penetration for all mixtures containing 1.5 and 3% decreased, though 3% was the best as the amount of decrease was 23.38 and 34.59 % for H1 and H2 mixture, respectively, as shown in Figure 5. This is due to the fact that CHNC reduced the pores in the concrete.

As for the percentage of 4.5%, despite the slight decrease in the depth of penetration as compared to the control mixture, its values were higher than those of the 1.5 and 3 % mixtures. This could be due the interaction of the halloysite with $Ca(OH)_2$ to form new products of C-S-H; an excess amount of silica would form, which would accumulate to form large granules distributed inside the concrete, weakening the bonding between the components of the matrix and thus adversely affecting the concrete [12]. This behaviour is close to the behaviour of nano silica.

As for mixture H3, each combination of halloysite and GGBS had a significant effect, reducing the depth of penetration by 19.62 mm with a decrease percentage of 36.69%. This is because both halloysite and GGBS have the ability to fill pores, in addition, halloysite reaction with $Ca(OH)_2$ which formed more C-S-H and the both effect means concrete very compact microstructure.

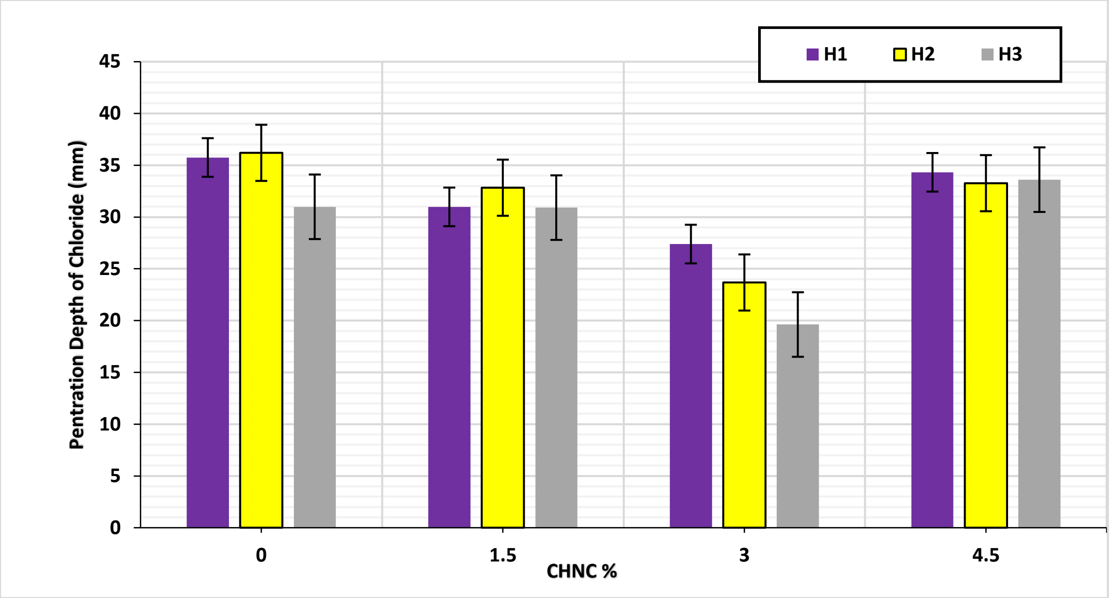

Figure.5: Depth Penetration of Chlorides for H1, H2 and H3 Mix

3.4.1. Weight Loss of Corroded Steel

After the chloride ions reached the steel rebar, the protective layer of concrete began to be destroyed. The surface of the steel turned into an anode electrode and the electrochemical reaction took place. This was followed by the corrosion of the steel, and it turned to a colour ranging from black to red rust. Pitting was also observed on its surface, as shown in Figure 6.

Figure 6: Corroded Steel Reinforcement

The weight loss of the steel sample provides a measure of the extent of corrosion that has occurred. The amount of weight loss in the reinforcing steel due to corrosion was determined by calculating the difference in weight between the initial weight of the steel sample and the weight after exposure to the corrosive environment. This weight loss can be calculated using the following equation 1

$$Loss\ in\ weight = \frac{Winitial - Wfinal}{Winitial} * 100$$

According to the findings of the study, the use of 3% of CHNC resulted in the lowest percentage of weight loss for all three concrete mixtures tested. This reduction in weight loss was particularly significant for mixtures H1 and H2, with a decrease of 41.30% and 49.74% respectively, while mixture H3 showed a decrease of 13.32% as shown in Figure 7. The results indicate that halloysite is effective in reducing pores and creating a dense matrix, which helps to preserve the reinforcing steel and reduce damage to the steel bar.

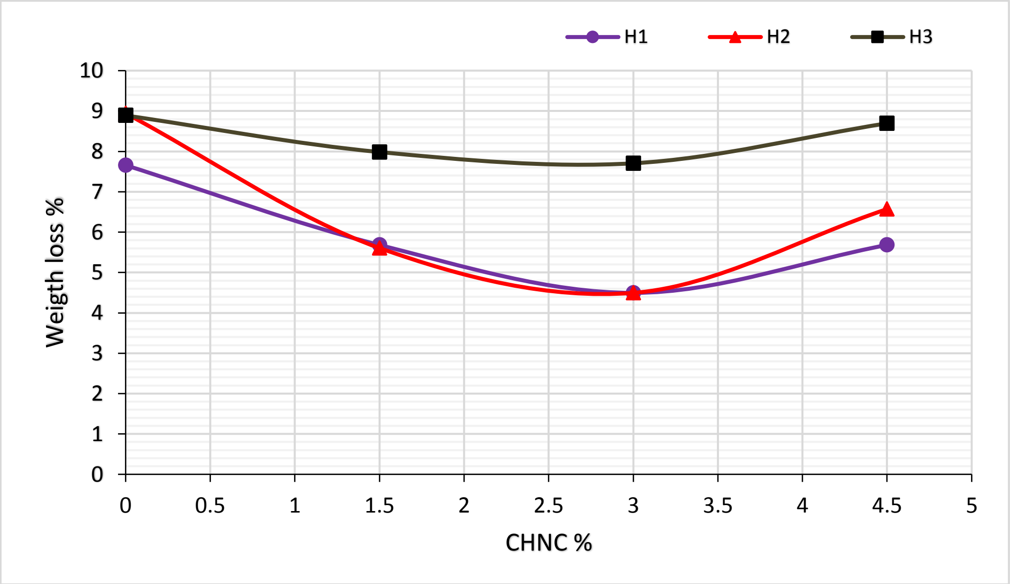

Figure7: Weight Loss of Steel Reinforcement

As a result of the corrosion process and the formation of rust, pressure is generated on the area surrounding the reinforcing steel and cracks form along the face of concrete parallel to the reinforcing steel. Cracks also form on the sides of the area surrounding the steel bar, as shown in Figure 8.

Figure 8: Crack Pattern for Concrete

Conclusion

This research shows the ability of halloysite to reduce the chlorides penetration in concrete. Penetration depth was measured by spraying silver nitrate on a sample that had been exposed to chlorides. The corrosion of the reinforcing steel was also predicted using an impressed current test, and the results were as follows:

1 -Halloysite is a kind of kaolin clay with an outer layer of silicon and a layer of aluminium interspersed with two layers of water .

2 -The results of the water absorption test for all concrete samples showed a decrease in the rate of water absorption and porosity; the halloysite worked to form additional gel products (C-S-H).

3 -The effect of halloysite on the migration coefficient at the age of 90 days was clearer than at the age of 28 days. The greater the replacement rate, the less the chloride was able to penetrate.

4 -According to the impressed current test, the depth of penetration of the chloride for all concrete mixes with 3% CHNC was the lowest.

5 -The lower the penetration depth of the chloride, the less weight was lost in the steel bar.

6- The corrosion process was accompanied by a change in the colour of the reinforcing steel to a black to red colour, and pits form on the surface of the reinforcing steel.

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دراسة تأثير مادة الهالويسايت النانو المكلسن على متانة الخرسانة تحت هجوم الكلوريد

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خلاصة

يشكل تأثير العوامل العدوانية، وخاصة الكلوريدات، على الهياكل الخرسانية تحديا كبيرا في مجال الهندسة. يؤدي وجود الكلوريدات إلى تآكل الخرسانة وتدهورها مما يؤثر على أدائها. تخترق الكلوريدات الخرسانة مما يؤدي إلى تدمير الطبقة الواقية حول حديد التسليح مما يؤدي إلى تآكل الفولاذ وتكوين الصدأ. يؤثر هذا التآكل سلبًا على قوة الارتباط بين الفولاذ والخرسانة ويمكن أن يسبب أيضًا تشققات على سطح الخرسانة، مما يقلل من متانتها. ولمواجهة هذا التحدي، تم إجراء دراسة بحثية لاستكشاف استخدام المواد النانوية، وتحديداً الهالويسايت المكلس النانوي، لتحسين أداء ومتانة الخرسانة. كان الهدف هو دراسة تأثير دمج الهالويسايت في الخرسانة على تغلغل الكلوريدات والتآكل اللاحق لقضبان حديد التسليح.

تم فحص ثلاثة خلطات خرسانية مختلفة تحتوي على نسب متفاوتة من الهالويسيت (١,٥%، ٣%، ٤,٥%). وقام الباحثون بتقييم معدلات امتصاص الماء ومعاملات الهجرة لهذه الخلائط. بالإضافة إلى ذلك، تم استخدام تقنية التيار المسلط، حيث تم تطبيق تيار ١٤ مللي أمبير لمدة ٢٦ يومًا لتسريع تآكل قضبان التسليح الفولاذية. أظهرت نتائج الدراسة فعالية دمج الهالويسيت في الخرسانة لتعزيز خواصه. حقق الخليط المحتوي على ٣% و٤,٥% من الهالويسايت (CHNC) الأهداف المرجوة، مما أدى إلى تقليل امتصاص الماء بشكل كبير. على سبيل المثال، أظهر الخليط الذي يحتوي على ٤,٥% (CHNC) انخفاضًا بنسبة ٤٢,٩٩% في امتصاص الماء بعد ٧ أيام. كما أدى هذا الانخفاض في امتصاص الماء إلى انخفاض كبير في معامل هجرة الكلوريدات واختراقها في الخرسانة. علاوة على ذلك، أدى إدراج ٤,٥% من الهالويسايت و٢٥% من خبث الفرن العالي المحبب (GGBS) في الخليط إلى تحسين أداءه.

الكلمة المفتاحية: الهالويسايت – متانة الخرسانة – تيار التأثير – معامل الإنتقال – الطين النانوي.