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Acidic Attack Resistance of Cement Mortar Treated with Alkaline

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Abstract

The negative effect of acidic attack on the properties of concrete and cement mortar is a topic of increasing significance in the recent years. Many attempts has occurred to mitigate this negative impact by improving the properties of concrete and increase resistance to acids by using additives. The present study includes treatment of sand by alkaline material and examine the effect of treatment on cement mortar resistance towards hydrochloric and sulfuric acid. Results show that sand treatment by alkaline material significantly enhance mortar ability to resist acids. In terms of loss weight, the maximum weight rate gain was 25.54% for specimens immersed in Hydrochloric acid with water cement ratio 40%. For specimens immersed in HCl, the average gain in compressive strength is (20.15-19.433)% for w/c (40-45)% respectively. The average gain in modulus of rupture toward the influence of H_2SO_4 is (18.37–17.29)% for w/c (40-45)%, respectively.

Keywords: Acidic resistance, Cement mortar, Flexural strength, Hydrochloric acid, Sodium hypochlorite, Sulfuric acid.

مقاومة مونة السمنت المعالجة بالمواد القاعدية للهجوم الحامضي

الخلاصة

إن التأثير السلبي للحوامض على خواص الخرسانة ومونة السمنت من الامور التي نالت اهتماما واسعا في السنوات الاخيرة من قبل المختصين في هذا المجال وقد ظهرت محاولات عديدة للتخفيف من هذا التأثير من خلال تحسين خواص الخرسانة وزيادة مقاومتها للحوامض باستخدام المضافات. تتضمن الدراسة الحالية معالجة الرمل بمادة قاعدية وقياس مدى تأثير هذه المعالجة على مقاومة مونة السمنت لحامضي HCl و H_2SO_4. اظهرت النتائج بأن هناك تأثيرا ايجابيا واضحا للمعالجة على مقاومة النماذج للحوامض. بلغت أقصى نسبة لزيادة مقاومة النماذج لتأثير حامض الهيدروكلوريك من ناحية النقصان بالوزن 25.54%. اظهرت النماذج ذات الركام المعالج والمغمورة في HCl زيادة في مقاومة الانضغاط مقارنة بنظيراتها ذات الركام غير المعالج بمعدل تراوح بين (20.15 – 19.433)% لنسبة ماء الى سمنت (40 - 45)% على التوالي. تراوحت نسبة زيادة معاير الكسر للنماذج ذات الركام المعالج تجاه تأثير H_2SO_4 بين (18.37 –17.29) % لنسبة ماء الى سمنت تراوح بين (40– 45)% على التوالي.

الكلمات الدالة: حامض الكبريتيك، حامض الهيدروكلوريك، مقاومة الحوامض، مقاومة الانثناء، مونة السمنت، هايبوكلورات الصوديوم.

Introduction

Concrete and cement mortar are considered as famous construction materials in the world and have various uses in engineering fields. Despite the good properties for them, they suffer weakness in some properties. Durability is an important property of concrete that acquire significant concern due to its clear effect on the service life of concrete structure. To reduce the deterioration of concrete and cement mortar different types of additives were used. These additives have proven their ability to improve the mechanical properties as well as to improve the chemical resistance. The chemical attack is considered of the most important reasons that lead to the deterioration of the concrete and cement mortar. According to ACI Committee Report 201, 2001[1], chemical attacks can be classified into several types that include; acidic attack, alkali attack, carbonation, chloride attack, leaching and sulfate attack. As a general rule acids can be considered deleterious to concrete. According to Reddy and Reddy, 2012[2], concentration of the acids and concrete permeability are the main factors contributing the concrete destruction. The negative effects of acids on concrete and cement mortar is related to the alkali nature of ordinary portland cement which makes it vulnerable to acid attack on account of high calcium hydroxides release during hydration of calcium silicate. The mechanism of degradation involves dissolution of soluble constituents of cement destroying its crystalline structure. It should be noted that the binder is damaged after acid attack. The chemical reaction can be expressed as follows;

1- Formation of Calcium Hydroxide

$$C_3S, C_2S + H_2O \rightarrow CSH + Ca(OH)_2 \ldots\ldots\ldots\ldots (1)$$

2- Reaction of Calcium Hydroxide

$$Ca(OH)_2 + \text{acid} \rightarrow Ca^2\ (solution) \ldots\ldots\ldots\ldots (2)$$

In 2009, Irassar[3], used sodium sulfate and magnesium sulfate as chemical solutions for immersion to study the extent to which the resistance of cement paste, mortar and concrete containing lime affected. The study concluded that reducing the water cement ratio increases the cubes resistance to salts. Mondal et al.[4], used rice husk ash (RHA) as an admixture in concrete and mortar specimens with partial replacement of cement by (0-20)%. The pure water and sulfuric acid of pH 2 and 3 were used to study the effect of acidic environment on compressive strength. The immersion period was ranging between (3–90) day. The study concluded that the strength of mortar decreases with age with increase in RHA in both acidic environments with lower decreasing rate in pH 3 than pH 2. In 2012 Quesalti and Duchenense[5], examined the effect of the nature of the supplementary cementing materials (SCMs) as well as curing time on the chemical and physical modifications of cement pastes and on the compressive strength, mass loss and microstructure of mortars immersed in acetic acid at pH of 4. The results showed that curing time before the acid immersion has beneficial effect, the metakaolin cement demonstrated and better durability and the slag cement exhibited good chemical resistance against acid attack. Rao et al.[6] , investigated the progressive deterioration of concrete mixtures containing various combination of fly ash through to expose the specimens to sulphate and chloride solutions of 5% concentration. The study concluded that in the ranges tested, the attack of H_2SO_4 on specimens is most severe and HCl is the mildest one.

Abdulla et al.[7] , studied the effect of treatment of porcelinite (used as fine aggregate) with alkaline solution (Sodium Hypochlorite) on the mechanical properties of cement mortar. The results showed that the mechanical properties of cement mortar was significantly improved and absorption of porcelinite stone was decreased while the density was increased by approximately 8%. In 2013, Abdulla[8], studied the impact of hydrochloric and sulfuric solvents and their combination on two types of lightweight concrete. The study produced that resistance of concrete increased when silica fumes was used, but it is not working always to increase concrete resistance to acids, especially when mixed with superplacticizer. The study proved that immersion of specimens in acidic solutions lead to decrease the compressive strength.

The present study aims to improve the resistance of cement mortar to acid attacks by using cheap and available alkaline solution (Sodium Hypochlorite). The properties improvement include study of the loss weight percentage in addition to the amount of change in compressive strength and modulus of rupture after immersion cement mortar specimens in hydrochloric and sulfuric acid for long duration.

Experimental Program

Materials

The details of materials used in this study are given below.

a- Cement: Iraqi ordinary portland cement conforming to the Iraqi standard specification (I.Q.S.No.5/1984)[9] was used. The chemical analysis and physical and mechanical properties are given in Table (1) below.

Table 1. Chemical and physical properties of cement used in study

Chemical analysis		
Constituent	Test results	I.Q.S. requirements
SiO_2	14.65	--------
Al_2O_3	5.38	--------
Fe_2O_3	3.3	--------
CaO	65.3	--------
SO_3	1.03	Max. 2.8%
MgO	2.45	Max. 5%
Loss on ignition	1.04	Max. 4%
Insoluble materials	1.01	Max. 1.5%
Lime Saturation Factor, L.S.F	0.9	(0.66 – 1.2)
C_3A	10.15	
physical and mechanical properties		
Specific surface area m^2/kg	299.75	250 m^2
Settling time, hr:min Initial Final	 0:54 7:15	 Min. 45 min Max. 10 hrs
Compressive strength, MPa, 3-days	33.89	Min. 15 MPa

b- Fine aggregate: Graded sand conforming to the Iraqi standard specification (I.Q.S.No.45/1984), zone 2 was used. The specific gravity is 2.6.

c- Acids: In this study two types of acids were used which are HCl and H_2SO_4 each of 5% concentration.

d- Alkaline solution: Sodium Hypochlorite (NaOCl) of 0.1 M, pH=11.8 and chorine ratio=1%.

Treatment Procedure

Sand used in this study was immersed in alkaline solution (NaOCl) for 24hrs and then washed and dried before using in preparation of specimens.

Preparation of Specimens

Two types of specimens have been prepared using the normal and treated sand labeled as N and T respectively. The cement:sand ratio was 1:2, water:cement ratios were (40, 42.5, 45)%. A total of 108 mortar specimens were cast in cube molds (50*50*50)mm and prism molds (40*40*160)mm. The notations used in this work are as following:

N: specimens with normal sand.

T:specimens with treated sand by alkaline material.

The numbers (40 , 42.5 and 45) after the notations indicate the water cement ratio (w/c). The additional notations (HCl and H_2SO_4) after N and T indicate that the type of acidic solutions. The number 28 after N and T indicates the age of specimens which used as reference specimens to show the effect of acidic solutions on specimens after the period of immersion (70 day).

Specimens Treatment and Test Procedure

Cement mortar specimens were demolded 24 hours after casting. At the end of curing period, 28 day, the specimens were taken out of water. For acid attack, for each type of specimens and water : cement ratio, 9 cubes and 9 prisms were taken and dried their surface by cloth, obtain their weights and recorded separately. Three cubes and three prisms were tested for 28 day compressive and flexural strength and the remaining were immersed in 5% solution of Hydrochloric and Sulfuric acid for 70 day to investigate the effect of acidic environments on loss weight percentage and residual compressive and modulus of rupture.

Results and Discussion

Loss Weight Percentage

Results show that specimens with treated sand demonstrated loss weight percentage less than specimens with normal sand. This is may be due to nature of alkaline material which increase the roughness of sand surface during treatment. The adhesion force between sand and cement mortar will be increased as a result of removing the material deposit inside the external micro pores of sand. The acidic solution will be kept out of concrete pore structure due to decreasing mortar porosity and permeability which lead to minimize the deterioration as much as possible depending on the acid type. Figures (1-8) show the behavior of specimens immersed in Hydrochloric and sulfuric acid during the study period. As can be noticed from these figures the great weight change percentage happened during the first two weeks for specimens immersed in Hydrochloric acid, while for specimens immersed in Sulfuric acid the weight change extended significantly for the first three weeks then decreased slowly.

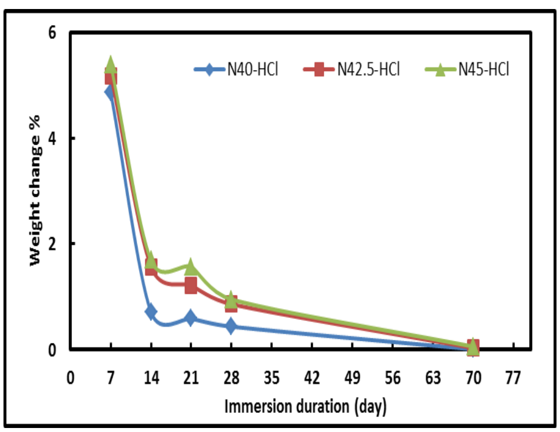

Fig.1. Variation of normal sand cubes weight change immersed in HCl with time

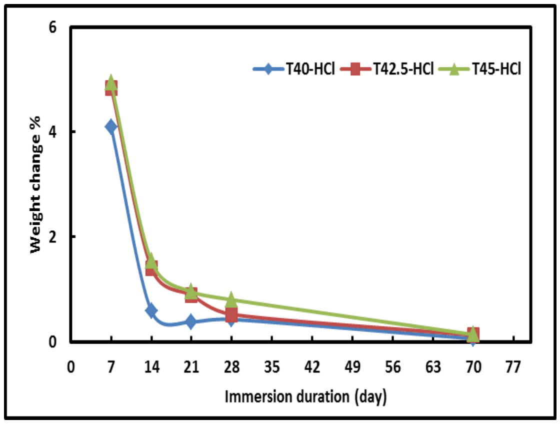

Fig. 2. Variation of treated sand cubes weight change immersed in HCl with time

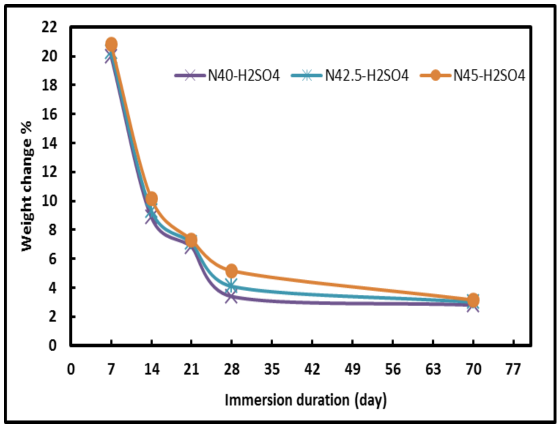

Fig. 3. Variation of normal sand cubes weight change immersed in H_2SO_4 with time

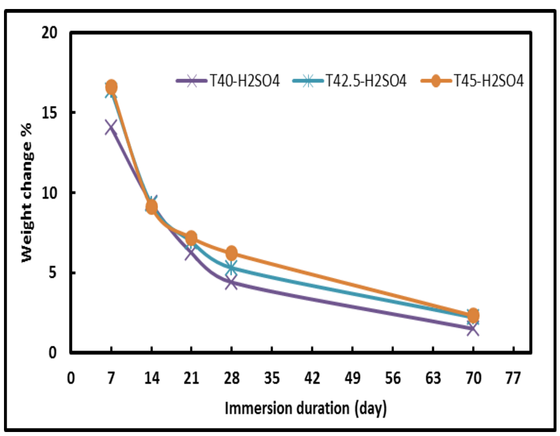

Fig. 4. Variation of treated sand cubes weight change immersed in H_2SO_4 with time

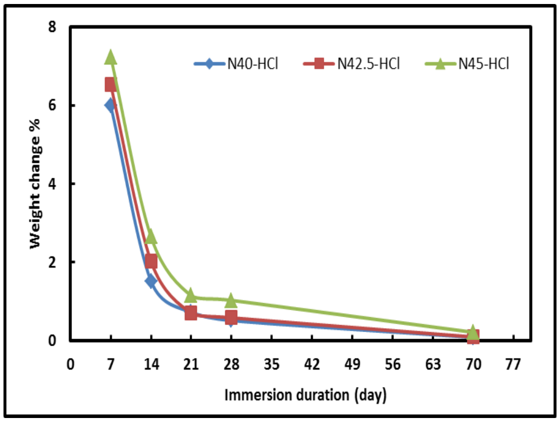

Fig. 5. Variation of normal sand prisms weight change immersed in HCl with time

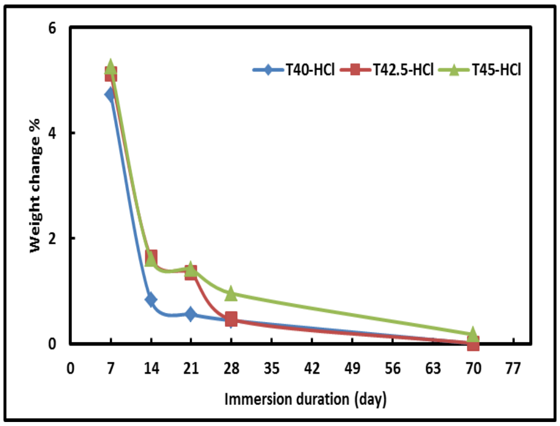

Fig. 6. Variation of treated sand prisms weight change immersed in HCl with time

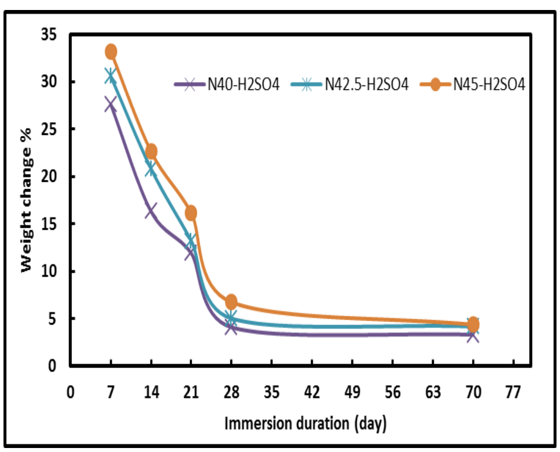

Fig. 7. Variation of normal sand prisms weight change immersed in H_2SO_4 with time

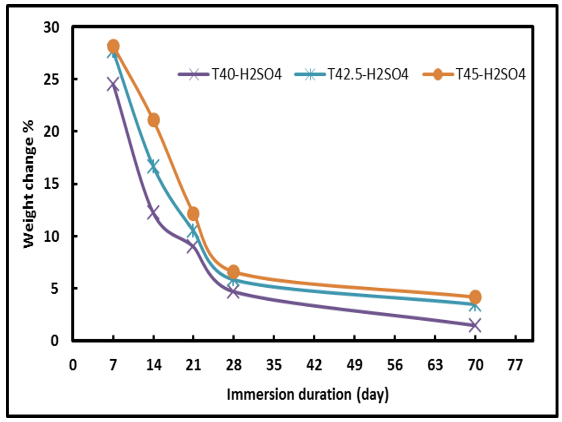

Fig. 8. Variation of treated sand prisms weight change immersed in H_2SO_4 with time

The following chemical equation presents the resulting products due to the action of HCl on cement hydration products, in particular calcium hydroxides[10].

$$Ca(OH)_2 + 2\,HCl \rightarrow CaCl_2 + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

From Equation (3) it can be seen that the salt of $CaCl_2$ is resulted from the consumption of $Ca(OH)_2$. Calcium chloride is a soluble salt and by the help of water may transport to the outer parts of mortars increasing the porosity and enlarge the capillary pores which lead to matrix deterioration, progressive microstructure breakdown and loss of mechanical strength. The loss weight of mortar specimens immersed in HCl happened rapidly in the first two weeks and then became slowly which means that the major quantity of calcium hydroxides is consumed during the first period.

In the case of sulfuric acid attack, the evaluation of deleterious reactions can be divided into two stages[11]. At the first stage, the expansive gypsum formation resulted from the deterioration of calcium hydroxide (CH) and calcium silicate hydrates (C-S-H). In aqueous environment, the gypsum will react with hydrated tricalcium aluminates (C_3A) to form ettringite ($C_6AS_3H_{32}$) and its analogs.

Monteney et al.[11] described the process by the following equations;

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O \ldots\ldots\ldots (4)$$

$$CaO\,.SiO_2.2H_2O + H_2SO_4 \rightarrow CaSO_4 + Si(OH)_2 + H_2O \ldots\ldots\ldots (5)$$

$$3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 14H_2O \rightarrow 3CaO.Al_2O_3 3CaSO_4.32H_2O \ldots (6)$$

Chemically, both gypsum and ettringite are defined with their low structure stability in comparison to the reactants they replace. They are also leading to reduce structure capacity because they are believed to cause expansion initiating cracks in structure[12].

Figure (9) shows that loss weight percentage for cubes specimens immersed in Hydrochloric acid is less than the corresponding specimens in sulfuric acid. The high C_3A content of cement makes mortar more susceptible towards Sulfuric acid attack[13,14], than Hydrochloric acid attack. The treatment of sand by alkaline solution leads to decrease the loss weight percentage for all specimens. for the same reasons mentioned above.

The maximum weight rate gain was 15.68% for specimens immersed in Hydrochloric acid with water cement ratio (40%). This might be connected to less permeability developed in specimens with low water/cement ratio which enhance the resistance towards acid.

Figures (10) and (11) show the effect of acids on normal and treated cement mortar cubes. Figure (12) shows loss weight percentage for prisms specimens due to immersion in acidic solutions. Treatment with alkaline solution leads to decrease the loss weight percentage for specimens with water cement ratio (40 – 45)% by (25.54 – 23.18)% and (17.88 – 12.99)% for Hydrochloric and Sulfuric acid respectively. Figure (13) shows the effect of acids on cement mortar prisms.

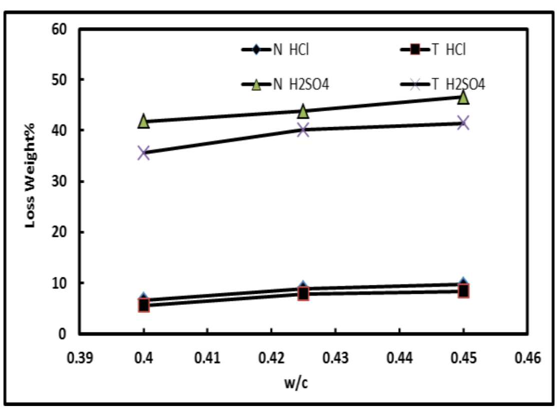

Fig. 9. Variation of cubes loss weight with w/c

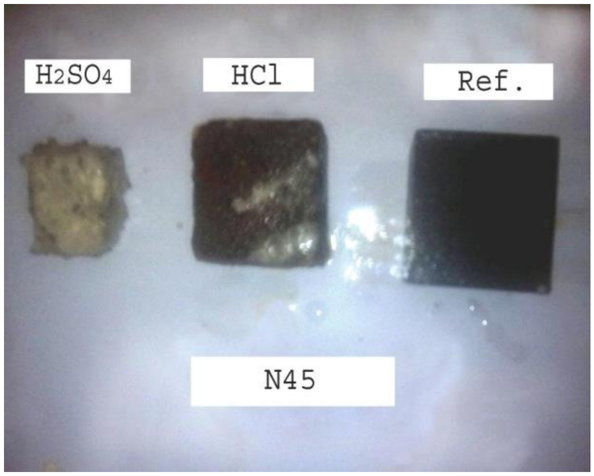

Fig. 10. Effect of acids on cube specimens with normal sand

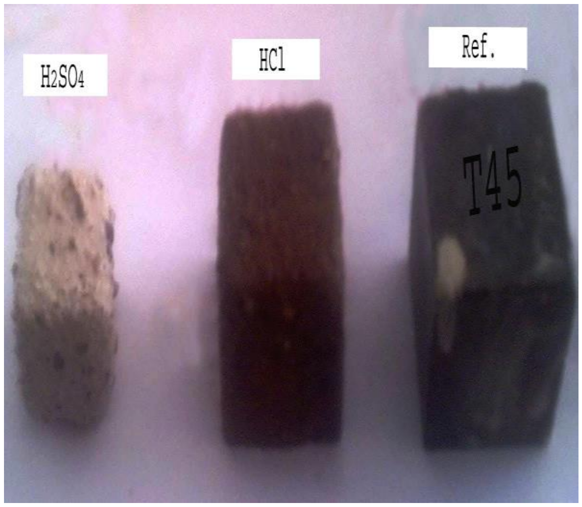

Fig.11. Effect of acids on cube specimens with treated

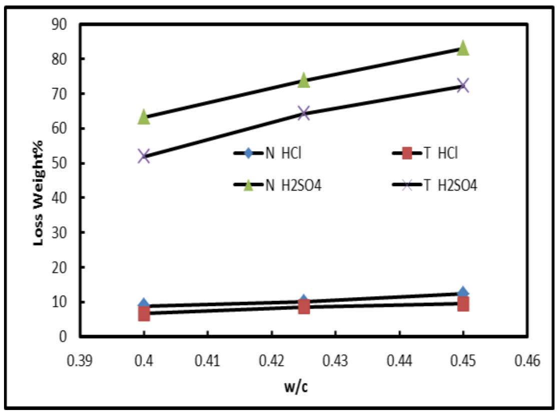

Fig.12. Variation of prisms loss weight with w/c

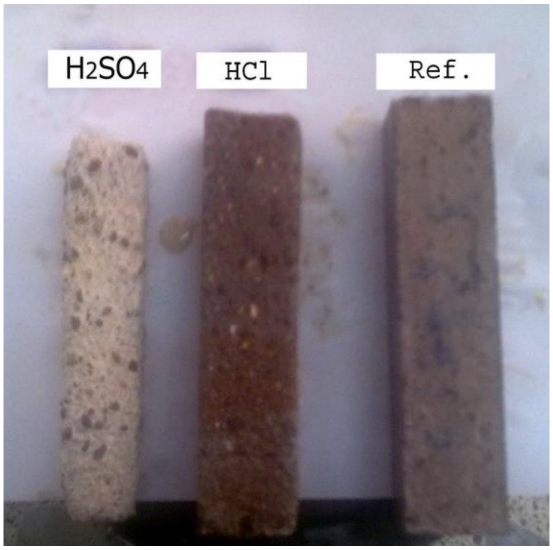

Fig. 13. Effect of acids on prism specimens

Compression Strength

The treatment of sand by alkaline solution increase the compressive strength in range of (23–19.75)% for water cement ratio (40–45)% respectively as shown in Figure (14). Sand treatment by alkaline decrease mortar porosity and permeability as a result of increasing the adhesion force between sand and cement mortar. Besides, the low water /cement ratio decrease the specimens permeability. These two factors give the superiority to the treated specimens with low water/cement ratio. The loss of compressive strength due to hydrochloric acid attack is (35.67–39.75)%, contracted due to sand treatment to (15.52–20.317)% for water cement ratio (40–45)% respectively. The treatment by alkaline reduces the matrix permeability and keep the acidic solution keep out, this will maintain the micro structure from destroying. The sulfuric acid attack is much severe as compared with hydrochloric acid. This result is similar to that was achieved by Rao, et al.[6]. The high C_3A content of cement makes mortar more susceptible towards sulfuric acid attack. The loss rate for sulfuric acid is (66.08–68.36)%. The corrosivity of sulfuric acid combined from sulfate ion participating in sulfate attack in addition to the dissolution caused by the hydrogen ion. Gypsum and ettringite which generated from the reaction described by Equations (4,5,6) above are defined chemically with their low structure stability in comparison to the reactants they replace. They are also leading to reduce structure capacity because they are believed to cause expansion initiating cracks in structure[12].

The gain in compressive strength due to sand treatment is (16.61–15.49)% for water cement ratio (40–45)% respectively. As expected w/c is an important parameter governing compressive strength so specimens with low water cement ratio exhibited lower loss in compressive strength because of its low permeability as compared with those of higher one. This is true for all the specimens tried in this study.

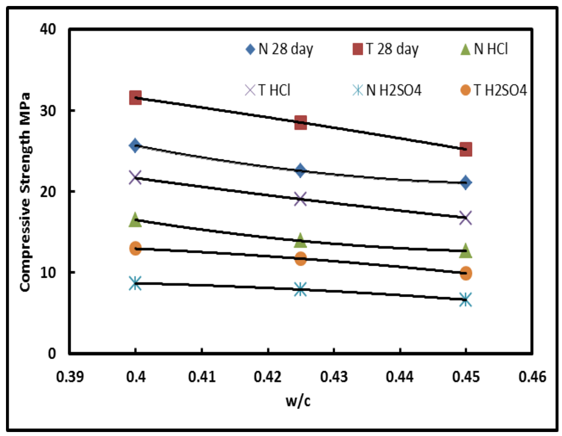

Fig. 14. Residual compressive strength

Modulus of Rupture

The variation of modulus of rupture (after 70 day immersion in acids) for different specimens is presented in Figure (15).

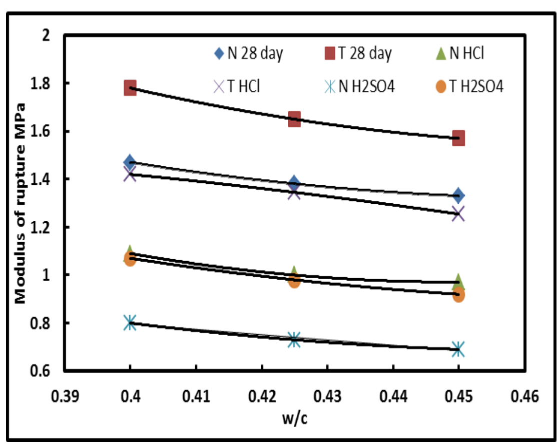

Fig. 15. Modulus of rupture for different specimens

The effect of sand treatment on modulus of rupture are presented in Figures (16-18). It can be noted from these figures that the specimens with treated sand demonstrated increasing in modulus of rupture as well as acidic resistance. This is due to the decreasing in permeability of mortar matrix which lead to enhance the mechanical strength of specimens.

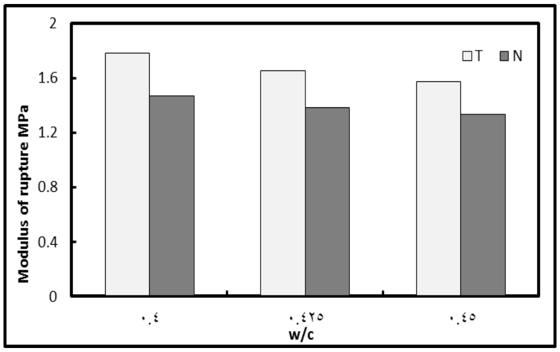

Fig. 16. Variation of modulus of rupture with w/c due to treatment

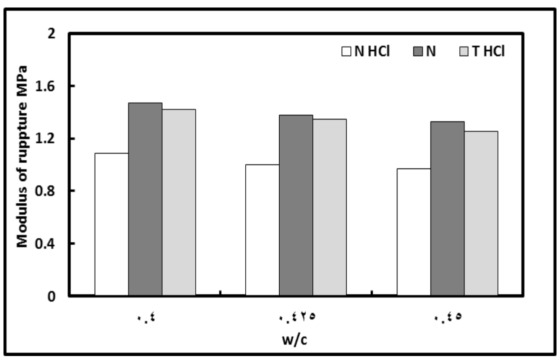

Fig. 17. Variation of modulus of rupture for specimens immersed in HCl with w/c

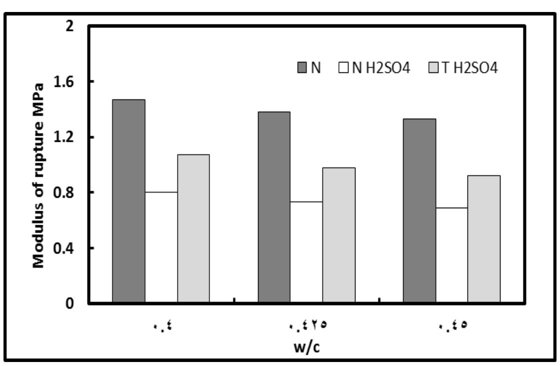

Fig. 18. Variation of modulus of rupture for specimens immersed in H_2SO_4 with w/c

As can be noted from the above figures specimens with low water/cement ratio exhibited higher values than these one with high water/cement ratio. The superiority results from low permeability which related to low water/cement ratio. This is also true for specimens immersed in both acids. To evaluate the acidic effect on specimens, we can see that specimens take the same trend that had been noticed when we discuss the results of compressive strength , (i.e. specimens produced from treated sand have higher acidic resistance as compared with those produced from normal one). Because of high C_3A content the specimens is more susceptible toward sulfuric acid than hydrochloric acid.

Conclusions

The present study establishes the superiority of specimens produced with treated sand to resist the acidic attack. The main important conclusions of the present study can be summarized below.

1- Treatment of sand with alkaline solution has significant role to improve the physical and mechanical properties of cement mortar due to reducing its permeability.

2- Attack of H_2SO_4 is more severe than HCl for all specimens on the ranges tested.

3- The compressive and modulus of rupture gain due to sand treatment is (23–19.75)% and (21.09–18.05)% for water cement ratio (40 – 45)% respectively.

4- The modulus of rupture gain for specimens with treated sand due to hydrochloric acid attack is (22.45–21.28)% for water cement ratio (40–45)% respectively. The corresponding ratios for sulfuric acid are (18.37–17.29)%.

5- The compressive strength gain for specimens with treated sand due to hydrochloric and sulfuric acid attack is (20.15–19.433)% and (16.61–15.49)% for water cement ratio (40–45)% respectively.

Recommendations

1- Investigate the acidic attack on cement mortar mechanical properties using non-destructive testing.

2- Investigate the effect of using the superplacticizer in addition to sand treatment by alkaline on cement mortar properties.
3- Investigate the effect of pozzolanic materials with treated sand on cement mortar acidic resistance.

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