IJE TRANSACTIONS C: Aspects Vol. 36 No. 12, (December 2023) 2198-2206

International Journal of Engineering

Journal Homepage: www.ije.ir

# Effect of Acidic Environments Containing Hydrochloric Acid on Rubberized Concrete

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*PAPER INFO*

*Paper history:*
Received 20 July 2023
Received in revised form 20 August 2023
Accepted 31 August 2023

*Keywords*:
*Recycled Materials*
*Compressive Strength*
*Admixtures*
*Curing*
*Hydrochloridric Acid*
*Environment*

*ABSTRACT*

Aggressive environment reduces the mechanical and durability-related properties of concrete. In this study, the effects of exposing the concrete containing crumbed tire rubber (CTR) to aggressive environmental conditions, including hydrochloric acid (HCl) is investigated. For this purpose, 5, 10, and 15% of the fine aggregate of the mixing design were partially replaced with the CTR, and then at the age of 7 days, when the concrete reached almost 70% of the initial strength, the samples were placed in water containing 2% HCl for 28 and 90 days. In this study, the effect of using Nano-$SiO_2$(NS) in the rubberized concrete and its behavior in acidic environments by replacing 5 and 10% by weight of cement with NS was also studied. Compressive strength and mass loss were evaluated at 28 and 90 days after casting. The results showed that the detrimental effects of HCl on the compressive strength of concrete significantly increased with an increasing in CTR content of concrete. The results also indicated that the impact of HCl acid on mass loss is improved by increasing the percentage of CTR so that the sample with the 15% crumbed tire showed a 7% lower weight reduction than the control sample.

***doi***: *10.5829/ije.2023.36.12c.09*

## 1. INTRODUCTION

The decline in performance, as well as the deterioration of concrete structures during the service life due to durability issues, cause high costs. Durability-related parameters, especially in corrosive environmental conditions, have a great impact on the final design of concrete structures. Many factors affect the durability-related properties of concrete that harmful chemical reactions are known as one of the most important factors of the gradual deterioration and reduction of performance of concrete structures.

The most important factors that cause destructive chemical reactions in concrete include carbonation, chloride ion penetration, alkaline reaction, acid attack, and sulfate attack [1]. Due to the high alkalinity of the concrete, it is easily vulnerable under acidic conditions [2]. Acid rain, industrial environments, and some groundwater, as well as wastewater treatment systems, are conditions that expose concrete structures to acids [3]. Estimates show that in some countries, the cost of repairing sewage systems that damaged by acid is higher than the cost of constructing new systems, which makes it necessary to study this effect on concrete structures more than ever [4].

Among the various acids, hydrochloric acid (HCl) and sulfuric acid are known as the most aggressive agents for concrete structure [5]. HCl is a staple and conventional acid in science laboratories and also it is one of the strong acids that can easily attack concrete. Physical and chemical reactions between acids and products due to the hydration of cement in concrete reduces the concrete performance [6]. The most important factors affecting the intensity of acid attack and the type of its mechanism are the coarse aggregate content, the type and composition of binder, the pH of the concrete environment, and the water to cement ratio [7, 8]. According to Chandra's [9] research, the HCl causes the formation of calcium-based salts soluble in water, and leaching out of these salts causes weakness in the structure of concrete. HCl accelerates the leaching process because of an increase in the

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Please cite this article as: S. A. Hosseini, F. A. Khankahdani, S. A. H. Moosavinezhad, Effect of Acidic Environments Containing Hydrochloric Acid on Rubberized Concrete, ***International Journal of Engineering, Transactions C: Aspects***, Vol. 36, No. 12, (2023), 2198-2206

calcium concentration gradient in the attacking fluid phase.

The production of cement and the extraction of concrete aggregates from natural resources cause environmental pollution as well as the waste of many natural resources. The use of secondary cementitious materials (SCM) or alternatives to aggregates has attracted the attention of many researchers [10]. These materials replace with some ingredients of concrete in a way that causes less harmful effects on the environment and in addition; improves some properties of concrete. Meanwhile, the reuse of recycled materials such as waste tires has received more attention because which if not used it will increase environmental pollution. Estimates show that millions of tires are worn out every year, and the lack of a proper technical and environmental method to destroy or recycle these tires has led to the accumulation or release of these tires in nature .

Recently, the use of waste tires as a partial replacement of concrete aggregates or as filler has been considered by many researchers [11, 12]. In addition to environmental benefits, improving the ductility of concrete is one of the most important reasons for using CTR in concrete [13]. Marques et al. [14] reported that the mechanical properties of concrete, such as compressive strength, are reduced by replacing 12% of fine aggregate with CTR at all ages. Al-Tayeb et al. [15] reported an improvement in the ductility of concrete containing up to 20% of the tire under impact loads. Holmes et al. [16] reported an increase in flexural strength due to the ductile behavior of this type of concrete by replacing 7% aggregate with the CTR. Pham et al. [17] reported the replacement of up to 15% aggregate with the CTR has almost no significant reducing effect on compressive strength; While in 30% replacement, there is a 40% reduction in the maximum load-carrying capacity of concrete samples. Overall, in most studies, the replacement of up to 15% of aggregate with CTR has had no impressive reduction in concrete strength [18, 19]. The reduction of bond strength between concrete and rebar, as well as the severe reduction of compressive strength when large amounts of crumb tire rubbers are used, are the most important disadvantages of using waste tires in concrete. The durability-related properties of rubberized concrete are not also well investigated. There are not many studies on the effect of acidic environments on the properties of concrete containing waste CTR. Segre et al. [20] reported good resistance of concrete containing 10% CTR in 5% HCl medium. Rashad [21] reported better behavior of concrete containing CTR than the plain concrete against HCl attack.

In addition to mechanical properties, durability-related properties of concrete containing CTR under the influence of various environmental factors has also been studied by some researchers. Ganesan et al. [22] investigated the effect of seawater and sulfuric acid solution on concrete samples containing 15% CTR and reported a greater mass loss of rubberized concrete than the control sample. By replacing different percentages of aggregates with crumb rubber obtained from PET bottles and storing samples in acidic environments, Shahini et al. [23] reported the appropriate behavior of samples containing crumb rubber. Avzedo et al. [24] reported an adverse effect under acidic conditions for concretes with different percentages of CTR but also concluded that water permeability properties remained constant for concrete containing up to 15% CTR. There has been a lot of research on the permeability of concrete containing CTR, and the results are very scattered. Pedro et al. [25] reported an approximately 9% reduction in water absorption in concrete mortars containing 5% CTR. Gesoglu et al. [26] reported a 44% reduction in the permeability of concrete containing 10% CTR. Hilal [27] has reported a 10% increase in water absorption for concretes containing 20% of CTR. Therefore, due to the dispersion in the results of previous research on the permeability of rubberized concrete, it is essential to study this issue.

Nano-$SiO_2$ (NS) is in the category of pozzolanic materials that adding it to concrete can improve the permeability properties as well as the strength of concrete [28, 29]. Pozzolans usually show their effects in improving concrete properties after a period of time due to their delayed reactions; However, due to the high intensity of NS pozzolanic reactions, concrete containing NS in the early days and during curing also has better strength and durability than conventional concrete [30]. NS improves strength by reacting with calcium hydroxide (CH) in concrete and producing calcium silicate hydrate (C-S-H), which is a more resistant material than calcium hydroxide [31]. Li et al. [32] reported the higher compressive and flexural strength of concrete containing NS than that of the control sample with the same w/b. Maghsoudi et al. [33] have reported a positive effect of adding NS against corrosion due to sulfate attack on concrete. Kumar et al. [8] replaced 2.5% of the cement with NS and cured concrete samples in a solution containing 5% HCl, reported that concrete containing NS was less corroded during 28 days of exposure to acidic conditions.

It is noteworthy that despite the extensive research done on concrete containing sub-tires, the available resources regarding the effect of corrosive environments, especially acidic conditions on this type of concrete are very limited. Considering that some investigations have considered the type of aggregate as effective on the performance of concrete against acid, replacing a part of aggregate with CTR can complement the study of the effect of concrete aggregate type in acidic conditions [34]. Additionally, it is desired to know more about this type of concrete for practical use in the road and construction industries, as well as the lack of regulatory criteria for this type of concrete, has necessitated the need for further evaluations. Considering that a way to improve the durability of concrete against acid attack is to improve its permeability; in this research, NS, which has the property of reducing the permeability of concrete, has been used. The available resources for the simultaneous effect of using tire and NS under acidic conditions are very limited. The effect of NS on this type of concrete, especially in acidic conditions, needs further investigation. In this research, the effect of exposing concrete containing CTR to HCl on compressive strength and mass loss of concrete has been investigated. In this study, the maximum percentage of aggregate replacement with CTR was limited to 15% [35]. Compressive strength and water permeability tests have been used to evaluate the mechanical properties and durability of concrete.

## 2. MATERIALS AND METHODS

Local ordinary type II Portland cement (OPC) complying with ASTM C150 was used as the binding material [36]. The NS with specific gravity of 2.35 and specific surface area of 185.5 ($m^2/g$) was used. The chemical compositions of OPC and NS obtained from XRF analysis are presented in Table 1. The fine aggregate was prepared from local rivers and the dolomitic limestone coarse aggregate was obtained from local mountain mines. Some mechanical properties of aggregates are shown in Table 2.

CTR with a maximum size of 5 mm and a specific gravity of 1.1 were prepared from a local recycling plant were used to replace part of the fine aggregate. In this research, the CTR was used to replace part of the fine aggregates, so the size range of CTR was chosen between 0.8-5 mm because this range is the commone particle size distribution of fine aggregate. The CTR was washed with potable water till their pH reached about tap water. Tap water complying with ASTM C1602 was used for casting

**TABLE 1.** Chemical compositions of OPC and Nono-$SiO_2$ by XRF analysis (wt.%)

| Chemical Composition | OPC | NS |
|---|---|---|
| CaO | 63.2 | 0.11 |
| $SiO_2$ | 22.6 | 98.73 |
| $Al_2O_3$ | 4.1 | 0.028 |
| $Fe_2O_3$ | 3.5 | 0.018 |
| $SO_3$ | 1.5 | 0.011 |
| MgO | 2.6 | 0.01 |
| $Na_2O$ | 0.2 | 0.2 |
| $K_2O$ | 0.5 | 0.01 |

**TABLE 2.** Mechanical proprties of aggregates

| Proprty | Fine | Coarse |
|---|---|---|
| Specific gravity | 2.85 | 2.61 |
| Water absorption | 1.07% | 2.36% |
| Fineness modulus | 2.63 | |

and curing of specimens [37]. The chemical compositions and physical properties of water are given in Table 3. HCl with a concentration of 98% was used. HCl concentration was reduced to the desired concentration of 2% based on the volume of water used to cure the samples.

The particle size distributions of fine and coarse aggregates after modification according to the ASTM C33 are shown in Figure 1 [38].

The control mix design was based on ACI standard with the water-to-binder ratio (w/b) equal to 0.4. In this study, 5%, 10%, and 15% of the volume of fine aggregate were replaced with CTR. In some mix designs, 5% and 10% of the cement were replaced with NS. Table 4 shows the mix proportions of the investigated concretes.

Various methods have been proposed by researchers and standards to evaluate the effect of the acidic

**TABLE 3.** Chemical and physical properties of mixing water

| Property | OPC | NS |
|---|---|---|
| $SO_4$ | 145 | mg/L |
| Cl | 62 | mg/L |
| TDS | 630 | mg/L |
| $CaCO_3$ | 415 | mg/L |
| $NO_3$ | 21 | mg/L |
| Na | 19 | mg/L |
| $K_2O$ | 0.5 | mg/L |
| Density | 1000 | $Kg/m^3$ |
| pH | 7.1 | |

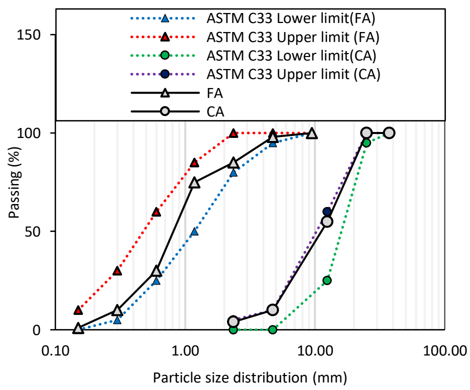


**Figure 1.** Particle size distribution of aggregates

environment on concrete. In most of the methods used by the researchers, the concentration of the acid has been different according to the purpose of the research. The concentration selected in this research was based on the conditions evaluated in the wastewater of an industrial complex.

By casting three samples for each experiment at each age, an appropriate number of 150 mm size cubes were cast for each mix design. To adjust the workability of concrete, its slump was kept within 10 cm by adding a carboxylate-based superplasticizer. After molding, the samples were kept at room temperature under plastic cover for 24 hours to retain moisture, and after demolding, they were cured with tap water for 7 days. After 7 days of standard curing, some samples were immersed in a solution with a concentration of 2% HCl and the rest were still kept under standard curing conditions.

For storage of samples, an anti-acid plastic tank with a volume of 500 liters, which contains 2% of HCl, was used. The tank water was changed every week to maintain the desired concentration of acid. Due to the errors caused by dissociating radicals on the pH value, the acid concentration was used to measure the acidity of the medium [39]. The temperature of water curing and acid solution was kept at level of 23°C ± 2°C [40]. After 28 and 90 days, the specimens were removed from the curing conditions and acid then the mass loss and compressive strength of the specimens were examined. The average of three specimens were used at every specified age and test.

**TABLE 4.** Concrete mix proportions per cubic meter of concrete

| Mix ID | Cement (kg) | NS (%) | CTR (kg) | CTR (%) | Fine Agg (kg) |
|---|---|---|---|---|---|
| T0N0(control) | 400 | 0 | 0 | 0 | 517 |
| T0N5 | 400 | 0 | 0 | 0 | 517 |
| T0N10 | 400 | 0 | 0 | 0 | 517 |
| T5N0 | 400 | 0 | 15 | 5 | 448 |
| T5N5 | 380 | 5 | 15 | 5 | 448 |
| T5N10 | 360 | 10 | 15 | 5 | 448 |
| T10N0 | 400 | 0 | 40 | 10 | 375 |
| T10N5 | 380 | 5 | 40 | 10 | 375 |
| T10N10 | 360 | 10 | 40 | 10 | 375 |
| T15N0 | 400 | 0 | 66 | 15 | 316 |
| T15N5 | 380 | 5 | 66 | 15 | 316 |
| T15N10 | 360 | 10 | 66 | 15 | 316 |

## 3. RESULTS AND DISCUSSION

**3. 1. Mass Loss** Mass loss of specimens was measured at 28 and 90 days after casting; for this purpose, at the desired age, the samples were removed from the solution and the corroded outer layer was separated with a soft brush. The specimens were stored in an oven at approximately 100°C and their weight was measured when the weight did not change with respect to time [41]. To obtain the mass ratio and evaluate the results, the weight of each specimen was divided by the weight of the 28-days water cured control specimen (without CTR and NS). Figure 2 shows the appearance of a specimen with CTR and the control specimen at the age of 28 days. The brown surface of the sample is attributed to the formation of ferric hydroxide [42].

Figures 3-5 show the mass ratios of samples at 28 and 90 days of curing and acid exposure conditions. Figure 3 shows the effect of different percentages of CTR on the weight of water-cured specimens; so that the effects of CTR and exposure conditions can be distinguished from the results presented in Figures 4 and 5. According to Figure 3, it is clear that NS has no effect on the weight ratio for water-cured specimens, and 5, 10 and 15% of

(a) Control specimen

(b) Specimen with 15% CTR

**Figure 2.** The appearance of samples after 28 days of exposure to HCl

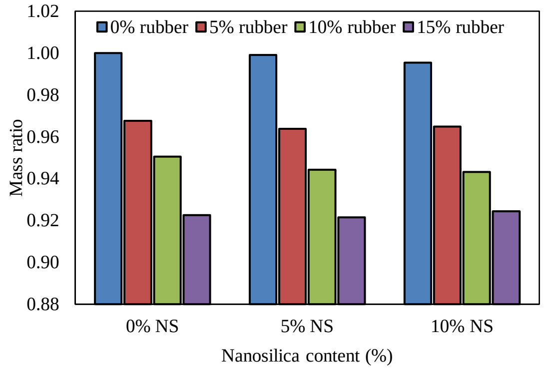


**Figure 3.** Mass ratio of water-cured specimens containing CTR and NS at 28 days

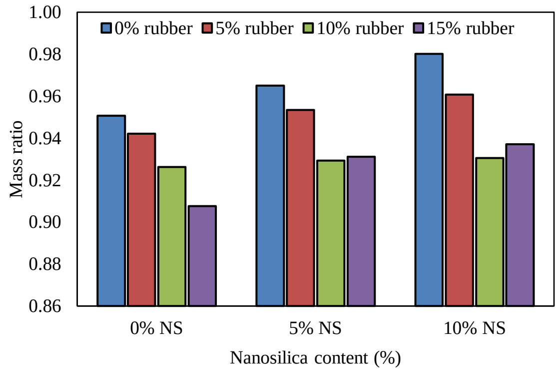


**Figure 4.** Mass ratio of specimens containing CTR and NS exposed to HCl at 28 days

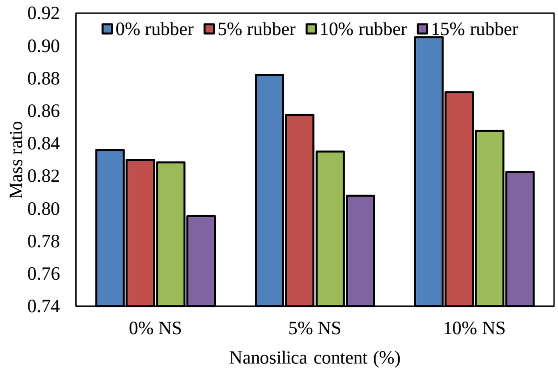


**Figure 5.** Mass ratio of specimens containing CTR and NS exposed to HCl at 90 days

the CTR has reduced the weight ratio to 0.97, 0.95, and 0.92 at the age of 28 days. As can be seen in Figure 4, for HCl exposure, the mass ratio for the T0N0 specimen reached 0.95 at 28 days, which means a 5% mass reduction of the control sample in an acidic environment. By adding 5 and 10% NS, the mass ratio has reached 0.96 and 0.98, which shows the positive effect of NS on weight loss values. For specimens with CTR in acidic conditions, less amount of mass loss was observed. The reason for this is that the CTR particles prevent peeling off the corroded outer layer and consequently prevent the spread of acid attack in the depth of the specimen .

As the age of the samples increased to 90 days, a greater decrease in the mass of the samples occurred; For the T0N0 sample, the mass ratio was reached 0.84 and for the T0N5 and T0N10 samples, the mass ratio has reached 0.88 and 0.91, respectively. At this age, due to the development of pozzolanic reactions, the effect of NS was more than specimens with 28 days' age. The positive effect of pozzolanic materials such as NS in reducing the effect of acid attack, especially mass loss of concrete due to HCl is comply to the results of most previous researchers. Goyal et al. [39] reported an approximately 13% reduction in the mass of the control sample exposed to 1% HCl and 8% reduction for concrete containing silica fume.

Figure 6 shows the effect of CTR and curing conditions on compressive strength at 28 and 90 days of age. To evaluate the strength ratio, the compressive strength of each specimen was divided by the compressive strength of the 28-day water-cured control specimen (without CTR and NS). From the results, it is clear that the strength ratio for specimens containing 5%, 10%, and 15% of the CTR under standard curing conditions was 0.94, 0.85 and 0.67, respectively. Exposure to HCl has caused these strength ratios reach 0.90, 0.81 and 0.58, respectively, which indicates the greater effect of acidic conditions on compressive strength with increasing CTR content of concrete. The reduction in compressive strength of the specimen without CTR with HCl exposure at 28 days of age was approximately 3%. As the age of the concrete increased to 90 days, the effect of HCl on the specimens increased. The sample containing 15% of CTR had a strength ratio of 45%. To understand how much of this reduction was due to the effect of the acid attack, the strength ratio of this sample in water-curing conditions should be considered. At the age of 90 days, the effect of acid attack

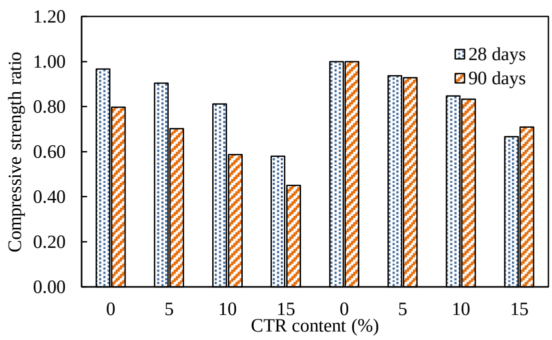


**Figure 6.** Strength ratio of specimens without NS at 28 and 90 days

has increased with increasing the percentage of CTR; for specimens containing 5%, 10% and 15% of CTR, the difference in resistance compared to water curing condition has reached to 23%, 25% and 27%, respectively.

The compressive strength of all specimens at age 28 days is illustrated in Figure7. Figures 8 and 9 show the

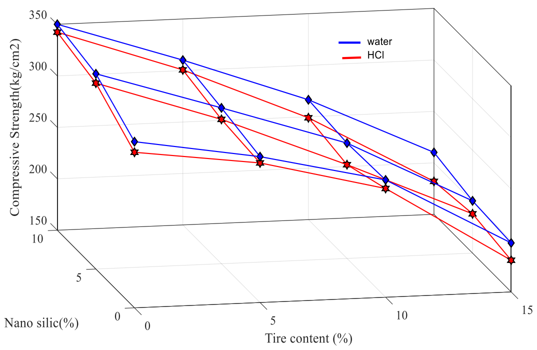


**Figure 7.** The compressive strength of the specimens at 28 days

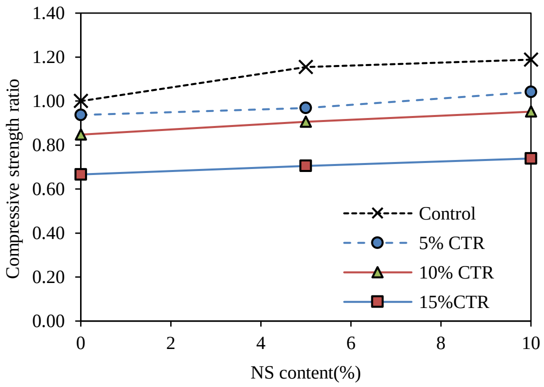


**Figure 8.** The compressive strength ratio based on CTR content and NS of water-cured specimens at 28 days

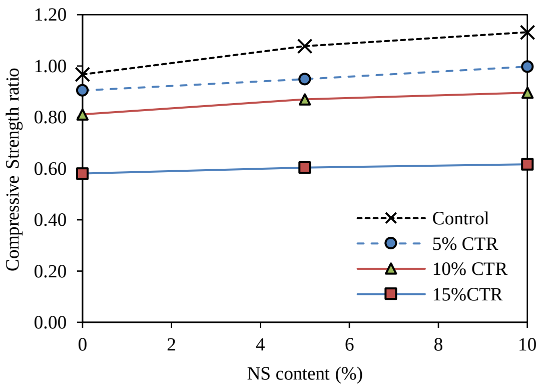


**Figure 9.** The compressive strength ratio based on CTR content and NS for HCl exposure conditions at 28 days

compressive strength ratio of the samples at 28 days for standard curing and exposure to HCl. The addition of NS in both conditions has improved the compressive strength. The compressive strength ratio for samples without CTR has reached 1.2 times that of the control sample by adding 10% NS at the age of 28 days. As can be seen from Figure 8 for the specimen, with 15% CTR, the strength ratio has increased from 0.67 to 0.74 with the addition of 10% NS. In any case, the addition of NS has improved the compressive strength, but the amount of this increase was less than the samples without CTR. In the case of exposure to hydrochloric acid, samples containing NS have reported more compressive strength, but with increasing the percentage of CTR, the effect of NS has been less.

As can be seen from Figure 10, with increasing the age of the samples to 90 days, the compressive strength of the T0N10 increased up to 20% compared to the control specimen at the same age. The compressive strength for this specimen, when exposed to HCl, was approximately equal to that of the Nano-free sample that was cured in water. T0N0 had a strength ratio of 0.8 and T0N10 had a strength ratio of 1.02, which shows the great effect of NS on improving the strength of samples exposed to HCl. In samples containing sub-tires at this age, the effect of adding NS was also positive, so that the strength ratio for samples containing 15% CTR increased by adding 10% NS from 0.45 to 0.57.

The effect of acids attack on concrete includes the dissolution of cement hydrates and calcium hydroxide and the formation of calcium salts [43]. HCl usually reacts with CH and has less effect on C-S-H. The resulting products react with calcium aluminate (C3A) in cement [44].

$$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \quad (1)$$

$$CaCl_2 + CaO.Al_2O_3 + 10H_2O \rightarrow 3CaO.Al_2O_3.CaCl_2.10H_2O \quad (2)$$

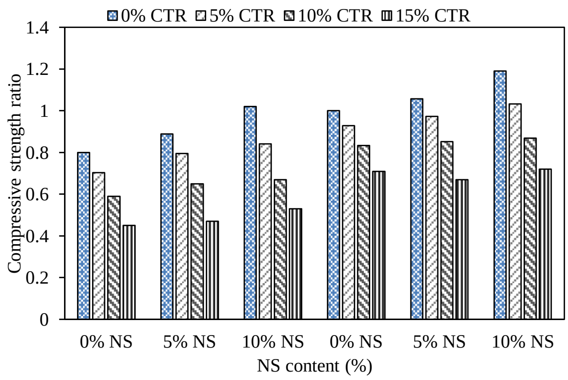


**Figure 10.** The compressive strength ratio based on CTR content and NS for HCl exposure conditions at 90 days

Products due to the effect of HCl on concrete include the formation of soluble and insoluble salts [9]. As shown in the reaction above, $CaCl_2$ is a water-soluble salt, and if, as in this experiment, the effect of acid on concrete was superficial, most of this salt will dissolve in water. Insoluble salts can reduce the permeability.

Concrete containing NS has a uniform and compact structure that reduces the permeability and increases the durability of concrete [45]. Due to their small size, NS fine particles play the role of filling effect well and therefore have a good effect in reducing permeability [43, 46]. The filler properties of nanoparticles also increase the strength of the final concrete structure. Pozzolanic reactions mostly involve the reaction of free hydrocalcium or CH, which is a hydration product, with NS [47]. These reactions result in the formation of C-S-H, which is a stronger substance in the concrete structure.

## 4. CONCLUSIONS

In this study, the effects of hydrochloric acid attack on the compressive strength and mass reduction of rubberized concrete with up to 15% of CTR were investigated, and based on the test results, the following conclusions can be drawn:

-Increasing the percentage of CTR increases the detrimental effects of hydrochloric acid on the compressive strength of the rubberized concrete so that for concrete with 15% CTR, the compressive strength at the age of 28 days is 10% and at the age of 90 days 26% less than concrete with the same percentage of CTR and cured with tap water.

- By increasing the percentage of crumbs, the effect of acid on weight loss is improved; The sample containing 15% of the tire had only 1.5% and the concrete without the CTR had 5% mass loss in 28 days compared to the equivalent sample cured in standard conditions.
- Adding NS improves compressive strength and decreases the samples' mass loss in aggressive environmental conditions containing HCl acid. Under hydrochloric acid attack conditions, the effect of NS on compressive strength is greater than mass loss such that for concrete, without CTR, up to 20% improves the strength of samples exposed to HCl.
- As a suggestion, concrete containing crumbed tire rubbers and also NS can be used in the flooring of industrial and laboratory environments containing hydrochloric acid.

## 5. ACKNOWLEDGMENTS

The authors would like to acknowledge the Savana Beton Company for material supplies and conducting tests.

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## Persian Abstract

**چکیده**

قرارگیری بتن در محیط‌های اسیدی موجب کاهش خواص مکانیکی و همچنین خواص مرتبط با دوام بتن می‌شود. در این مقاله اثر قرارگیری بتن حاوی خرده تایر در شرایط محیطی خورنده حاوی اسید هیدروکلریدریک مورد مطالعه قرارگرفته است. بدین منظور در طرح اختلاط‌های مختلف، مقدار ۵، ۱۰ و ۱۵ درصد از ریزدانه بتن با خرده تایر جایگزین شده و بعد از ۷ روز عمل آوری در شرایط استاندارد و رسیدن به ۷۰ درصد مقاومت طرح، نمونه‌ها در محیط حاوی ۲ درصد اسید هیدروکلریدریک قرار داده شدند. در برخی از نمونه‌ها برای بررسی اثر نانو سیلیس بر مقاومت بتن در برابر اسید، مقدار ۵ و ۱۰ درصد سیمان با ژل نانو سیلیس جایگزین گردید. بعد از ۲۸ و ۹۰ روز قرار گیری در شرایط اسیدی، مقاومت فشاری و کاهش وزن نمونه‌ها مورد بررسی قرار گرفت. نتایج نشان داد که در نمونه‌های با خرده تایر بیشتر، اثرات کاهشی اسید هیدروکلریدریک بیشتر بوده است. بر اساس نتایج بدست آمده همچنین مشخص شد که مقدار خوردگی (کاهش وزن نمونه‌ها) با افزایش درصد خرده تایر بهبود یافته است به طوریکه نمونه حاوی ۱۵ درصد خرده تایر تا ۷ درصد کاهش وزن کمتری نسبت به نمونه شاهد داشته است.