Chloride Diffusion and Acid Resistance of Concrete Containing Zeolite and Tuff as Partial Replacements of Cement and Sand

Ehsan Mohseni [1], Waiching Tang [1,*] and Hongzhi Cui [2]

[1] School of Architecture and Built Environment, The University of Newcastle, Callaghan NSW 2308, Australia; Ehsan.Mohseni@uon.edu.au
[2] Shenzhen Durability Center for Civil Engineering, Shenzhen University, Shenzhen 518060, China; h.z.cui@szu.edu.cn
* Correspondence: patrick.tang@newcastle.edu.au; Tel.: +61-2-4921-7246

Abstract: In this paper, the properties of concrete containing zeolite and tuff as partial replacements of cement and sand were studied. The compressive strength, water absorption, chloride ion diffusion and resistance to acid environments of concretes made with zeolite at proportions of 10% and 15% of binder and tuff at ratios of 5%, 10% and 15% of fine aggregate were investigated. The results showed that the compressive strength of samples with zeolite and tuff increased considerably. In general, the concrete strength increased with increasing tuff content, and the strength was further improved when cement was replaced by zeolite. According to the water absorption results, specimens with zeolite showed the lowest water absorption values. With the incorporation of tuff and zeolite, the chloride resistance of specimens was enhanced significantly. In terms of the water absorption and chloride diffusion results, the most favorable replacement of cement and sand was 10% zeolite and 15% tuff, respectively. However, the resistance to acid attack reduced due to the absorbing characteristic and calcareous nature of the tuff.

Keywords: zeolite; tuff; durability; acid attack; chloride ion diffusion

1. Introduction

Today, concrete is the most used man-made material in the world due to its competitive price and desirable properties. However, cement production is estimated to produce about 5% to 7% of total greenhouse gas emission each year. This has a significant impact on the environment and construction industries [1]. The high carbon footprint of cement production urges the industry to look for more sustainable, durable and low-energy products. Nowadays, supplementary cementing materials (SCM) have been widely used to reduce the consumption of Portland cement in order to improve the sustainability of our environment [2–5]. SCM can be categorized into two main groups: natural pozzolans (e.g., volcanic ash, volcanic tuff, pumice or burned clay); and artificial pozzolans (e.g., silica fume, fly ash, metakaolin etc.) [2–5]. SCMs are usually added to concrete to reduce permeability, increase strength, or to provide a sustainable solution where a large amount of binder is required [6]. Zeolite is a marvelous mineral SCM containing large amounts of SiO_2 and Al_2O_3, which are responsible for the pozzolanic activity of zeolite.

In many countries, such as Russia, Germany, Slovenia, Spain, China, Turkey and Iran, Zeolites have been used successfully in concretes providing both technical and environmental advantages over conventional Portland cement concrete. Some of the advantages that make zeolite an acceptable SCM in construction include: good physical properties (high surface area, high cation exchange capacity

and porosity), strong chemical properties (high reactive SiO_2 and Al_2O_3 contents), environmental advantages (Cr^{6+} adsorption, anti-bacterial agent, humidity-conditioning material), and economic advantages (high reserves and low cost of production) [7].

The impact of zeolite on concrete properties has been investigated in previous research. Chan et al. [8] reported that concrete specimens that incorporated 15% zeolite showed high compressive strength values ranging from 97 MPa to 110 MPa. Ahmadi et al. [9] also found that the optimum percentage of zeolite was 15% when the water-to-binder ratio was equal to 0.4. Poon et al. [10] assessed the impact of zeolite in cement pastes. Their results showed that the inclusion of natural zeolite contributed to strength development of cement pastes. Valipour et al. [11] found that concrete containing 10% zeolite displayed acceptable durability properties and mechanical performance. Najimi et al. [12] reported that concrete with 15% zeolite gave the best results in terms of compressive strength, water absorption and chloride ion penetrations. However, the specimens did not show satisfactory results against acidic environments. In another study by Najimi et al. [7], natural zeolite was found to be more effective than silica fume in self-consolidating high performance concrete. Considering the advantages in terms of availability and cost-effectiveness, natural zeolite can be considered to be a promising SCM [13].

On the other hand, over the last few decades the increase in demand for sand for the rapid increase in construction activities (e.g., large housing programs and infrastructures) has placed immense pressure on this valuable resource. To overcome this problem, it is crucial to use substitute materials such as crushed sand, dune sand, limestone fines, natural pozzolana, blast-furnace slag and different wastes. However, with these palliative materials, the market expectations are still far from being satisfied. Consequently, research on other replacements would be required.

Tuff is usually lighter than aggregates such as sand, gravels and ground rocks [14,15]. There has been little research reported on the use of tuffs in structural concrete. Tuff is usually used as a sand replacement to make the resulting concrete considerably lighter than normal concrete. In some previous research, tuff was used as a lightweight expanded aggregate (LEA). Yasin et al. [16] investigated the effect of three different types of volcanic tuff (yellow, grey and brown) as fine aggregate. They concluded that replacing 20% of fine aggregate with brown or grey tuff improved the concrete compressive strength by 10%, and 15% when yellow tuff was used. Al-Zou'by et al. [17] investigated the impact of replacing sand with different levels of tuff replacement (25%, 50%, 75%, and 100% by weight) on concrete. Their results showed that the compressive and flexural strengths of samples containing 50% tuff increased significantly. They also shown that the unit weight of concrete decreased with the increase of volcanic tuff. Based on their results, the use of volcanic tuff also improved the mechanical properties of cement mortar specimens. Abil et al. [18] studied the effect of using blends of volcanic tuff (VT) and fly ash (FA) as a partial cement replacement on concrete, and indicated that the 28-day compressive strength of specimens containing 12% VT and 10% FA was about 7% less than the control concrete.

Concrete is a susceptible material to acid attack [19]. Concrete can be attacked by acids both internally and externally. The existence of different kinds of acid in the environment around the concrete causes a great reduction in the pH of the concrete, and the reaction between the acids and the hydrated and unhydrated cement finally leads to the deterioration of the concrete. The primary effect of any type of acid attack on concrete is the dissolution of the cement paste matrix.

Portland cement concretes usually do not have a high resistance to acid. Acids attack concrete by dissolving both hydrated products and unhydrated cement as well as calcareous aggregates. Concrete deterioration increases as the pH of the concrete decreases due to the acidic environment. Sulphuric acid can exist in many different places, such as:

(i)   Places where industrial waste exists. Industrial waste may often contain a large amount of sulphuric acid. The sulphuric acid in industrial waste may cause severe corrosion in concrete pipes in the short or long term period.

(ii)   Groundwater normally contains different kinds of sulfates, and free sulfuric acid may also be one of the products.

(iii)   Acid rain, which is formed by oxidation of sulfur dioxide, is a product of the combustion of coal and petroleum or other industrial processes. Acid rain decreases the pH of the concrete significantly and results in deterioration of concrete.

In the literature there is no research on examining the effect of both tuff as fine aggregate and zeolite as SCM together on durability of concrete or on its resistance against different hazardous acids. This research aimed to study the influence of tuff and zeolite on strength development, water absorption, chloride penetration and acid resistance properties of concrete samples.

2. Materials and Methods

2.1. Materials

Portland cement Type I complying with the requirement of ASTM C150 was used. Tuff and zeolite were obtained from the same volcanic areas of the northern region of Iran. Chemical compositions and physical properties of the cement, zeolite and tuff are given in Table 1. The mineral compounds of zeolite are clinoptilolite (73%), opal CT (17.2%), quartz (1.5%), plagioclase (2.1%), k-feldspar (1.3%) and smectite/illite (clay minerals) (4.9%). Clinoptilolite can absorb a wide range of toxins and heavy metals. It can also be successfully used in the production of molecular sieves due to its unique crystalline structure [20].

Table 1. Chemical composition and physical properties of cement, zeolite and tuff.

	Constituents (wt. %)	Cement	Zeolite	Tuff
Chemical composition	SiO_2	21.75	69.2	60.31
	Al_2O_3	5.15	15.28	17.36
	Fe_2O_3	3.23	3.01	5.24
	CaO	63.75	2.24	5.95
	MgO	1.18	1.4	1.56
	SO_3	1.97	0.45	0.41
	K_2O	0.56	2.1	3.01
	Na_2O	0.33	2.2	2.58
	Loss on ignition	2.08	4.12	3.58
Physical properties	Specific surface (m^2/g)	0.33	0.31	0.45
	Specific gravity	3.15	2.24	1.95

Natural river sand with water absorption of 1.2% and a nominal maximum particle size of 4.75 was used as fine aggregate. Tuff with similar particle size distribution was used for partial replacement of fine aggregate. The fineness modulus of sand and tuff lay between 2.7 and 2.8, which indicated that they were medium-coarse. Limestone gravel with water absorption of 0.69% and a nominal maximum size of 12.5 mm was used as coarse aggregate. Table 2 shows the physical properties of the aggregates used in this study. Due to the high absorption characteristics of tuff, the tuff particles were pre-wet before mixing the concretes. For manufacturing lightweight aggregate concrete, there is a mature pre-wetting method in the concrete industry. The pre-wetting method employed in this research is the same as that used for the authors' previous research [21,22]. After pre-wetting, the aggregates were dried using a large cloth until all the water on the aggregate surface was removed so that the aggregates were in a saturated surface-dried condition prior to concrete mixing. Polycarboxylic ether-based high-range water reducer (HRWR), namely Glenium 51, with a density of 1.08 g/cm^3 was used to achieve the flowability of the mixtures. Sulphuric acid with 98% concentration and hydrochloric acid with 37% concentration were used to make an acidic solution of 5% concentration.

Table 2. Properties of sand, gravel and tuff.

	Sieve Opening	Cumulative Passing (%)		
		Sand	**Gravel**	**Tuff**
Gradation	1/2 in. (12.5 mm)	-	95	-
	3/8 in. (9.5 mm)	-	49.2	-
	No. 4 (4.75 mm)	96	8.23	98
	No. 8 (2.36 mm)	82.4	3.3	89
	No. 16 (1.18 mm)	68.2	-	72.1
	No. 30 (600 μm)	42.5	-	44.4
	No. 50 (300 μm)	20.7	-	18.8
	No. 100 (150 μm)	6.9	-	7.7
Maximum nominal size (mm)		4.75	12.5	4.75
Fineness Modulus		2.8		2.7
Specific gravity		2.65	2.6	2.1
Water absorption (%)		1.2	0.69	16

2.2. Production of Specimens

In this experiment, a total of 10 different concrete mixtures were made. Tuff was added at the ratios of 5%, 10% and 15% (by weight) as partial replacement of sand and zeolite was used at 10% and 15% (by weight) as replacement of cement. The water-to-binder ratio was 0.4 and kept constant for all mixtures. The abbreviations for the labeling of the mixtures used in this study are adopted in such a way that the number after T shows the percentage of tuff and the number after Z shows the percentage of zeolite. The mixture proportions of the specimens are presented in Table 3.

Table 3. Mixture proportions of the specimens.

Mix ID	Cement (kg/m^3)	Water (kg/m^3)	Zeolite (kg/m^3)	Tuff (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)	HRWR (kg/m^3)
Control	550	220	0	0	880	755	3
T5	550	220	0	44	836	740	4
T10	550	220	0	88	792	725	4
T15	550	220	0	132	748	710	5
T5Z10	495	220	55	44	836	720	4
T5Z15	467.5	220	82.5	44	836	715	4
T10Z10	495	220	55	88	792	700	4
T10Z15	467.5	220	82.5	88	792	695	4
T15Z10	495	220	55	132	748	690	5
T15Z15	467.5	220	82.5	132	748	685	5

The mixing procedure used by Khayat et al. [23] was utilized for making the samples. First, the fine and coarse aggregates and tuff (if applicable) were mixed for 30 s at a normal mixing speed of 80 rpm. Then, half of the mixing water was added and mixed for 1 min. Thereafter, cement and/or zeolite were added and mixed for one more minute. The remaining water and HRWR were then added and mixed for 3 min. Eventually, after 2 min of rest, mixing was done for additional 2 min. This optimum time is necessary to disperse the HRWR and stabilize the viscosity. The mixtures were then poured into cubic molds of 10 cm × 10 cm × 10 cm for different tests. All samples were cured in water at a temperature of 23 ± 2 °C and until they were tested.

2.3. Testing of the Specimens

Compressive strength was tested in accordance with IS 516 [24] at 28, 90 and 236 days of age. In this test, cube specimens were cured in water at a temperature of 23 ± 2 °C until they were tested. The rate of loading was 13.72 MPa per minute.

The water absorption of hardened concrete was determined in accordance with the ASTM C642-13 standard [25]. Water absorption testing was conducted at an age of 90 days. In this test, the specimens were dried in an oven at $110 \pm 5\,^{\circ}\text{C}$ for 24 h. After that, they were weighted and immersed in water at $21\,^{\circ}\text{C}$ for 48 h. Then, they were weighed again and this sequence was repeated until the difference between the values obtained from two successive values of mass was less than 0.5% of the lesser value. The water absorption was then calculated using Equation (1)

$$\text{water absorption} = (B - A)/A \times 100\ (\%) \tag{1}$$

where A and B were the weights of the sample in dried and SSD conditions respectively.

Chloride diffusion testing was conducted on specimens after 90 days of curing according to ASTM 1556-11a Standard [26]. In this test, the specimen was immersed in a saturated calcium hydroxide water bath in 24 h. Then the specimen was removed, rinsed and placed in exposure to sodium chloride solution (an aqueous NaCl solution prepared with a concentration of 165 ± 1 g NaCl per L of solution) at a temperature of $23 \pm 2\,^{\circ}\text{C}$. The specimen remained in the exposure of the liquid for 90 days. Then the specimen was removed from the liquid, rinsed with water and dried in laboratory air at $23 \pm 2\,^{\circ}\text{C}$. Later, the powder sample was obtained by grinding off the material in layers parallel to the exposed surface. At least 10 g of sample was obtained. Finally, the chloride diffusion coefficient was calculated using Equation (2)

$$C(x,t) = C_s - (C_s - C_i) \cdot erf\left(\frac{x}{\sqrt{4 \cdot D_a \cdot t}}\right) \tag{2}$$

where, $C(x,t)$ = chloride concentration, measured at depth x and exposure time t, mass %, C_s = projected chloride concentration at the interface between the exposure liquid and test specimen that was determined by the regression analysis, mass %, C_i = initial chloride-ion concentration of the cementitious mixture prior to submersion in the exposure solution, mass %, x = depth below the exposed surface (to the middle of a layer), m, D_a = chloride diffusion coefficient, m^2/s, t = the exposure time, s, and erf = the error function.
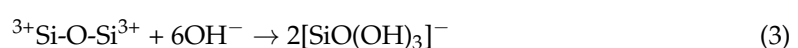
Sulphuric acid attack and hydrochloric acid attack tests were conducted on hardened concrete samples at an age of 56 days. The concentration of the acid solution was kept constant at 5% by regularly adjusting the pH of the solution. Samples were immersed in sulphuric or hydrochloric acid solution for 180 days at a temperature of $23 \pm 2\,^{\circ}\text{C}$, thereafter, the samples were taken out and assessed visually. At the same time, compressive strength of specimens was measured. After leaving specimens in the oven at $100\,^{\circ}\text{C}$ for 24 h, the samples were weighted to measure the mass loss.
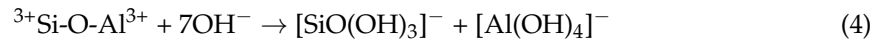
3. Results and Discussion

3.1. Compressive Strength

Compressive strength values of the concrete samples at 28, 90 and 236 days of age are presented in Figure 1. It can be seen that the strengths of concrete samples containing tuff and zeolite were higher than those of the control samples at all ages. The most positive effect on strength was noted for 15% tuff, while compressive strength further increased when zeolite was used to replace cement. The optimum replacement percentage of zeolite was found to be 10%, but samples with 15% zeolite experienced a small decline in strength. The fractured surface of a sample containing 10% zeolite and 15% tuff after the compressive strength test is shown in Figure 2. The strength enhancement is mainly due to the acceleration of pozzolanic activity of samples with tuff and zeolite which can be explained as follows [27]:

1.　By mixing water and a $Ca(OH)_2$-pozzolan blend, the $Ca(OH)_2$ hydrolysed, which resulted in a high pH value. Then the silicate or aluminosilicate network of the pozzolanic material was broken down due to the OH^- attack, and the depolymerized species entered the solution as follows:

$$^{3+}\text{Si-O-Si}^{3+} + 6OH^- \rightarrow 2[\text{SiO(OH)}_3]^- \tag{3}$$

$$^{3+}Si\text{-}O\text{-}Al^{3+} + 7OH^- \rightarrow [SiO(OH)_3]^- + [Al(OH)_4]^- \qquad (4)$$

By means of the connection of Ca^{2+} ions and the above products (i.e., the dissolved monosilicates and aluminate types), crystalline calcium silicate and aluminate hydrate were created that were similar to those present in the hydration of cement. Such synthesized products tended to harden, and consequently, they promoted the increase in mechanical strength of the cementitious material. Besides, the crucial environmental and economic merits of zeolite should not be neglected, since the production of cement needs a lot of energy input which results in high CO_2 release in the atmosphere.

2. The high surface area of tuff accelerated the hydration rate and resulted in higher compressive strength.
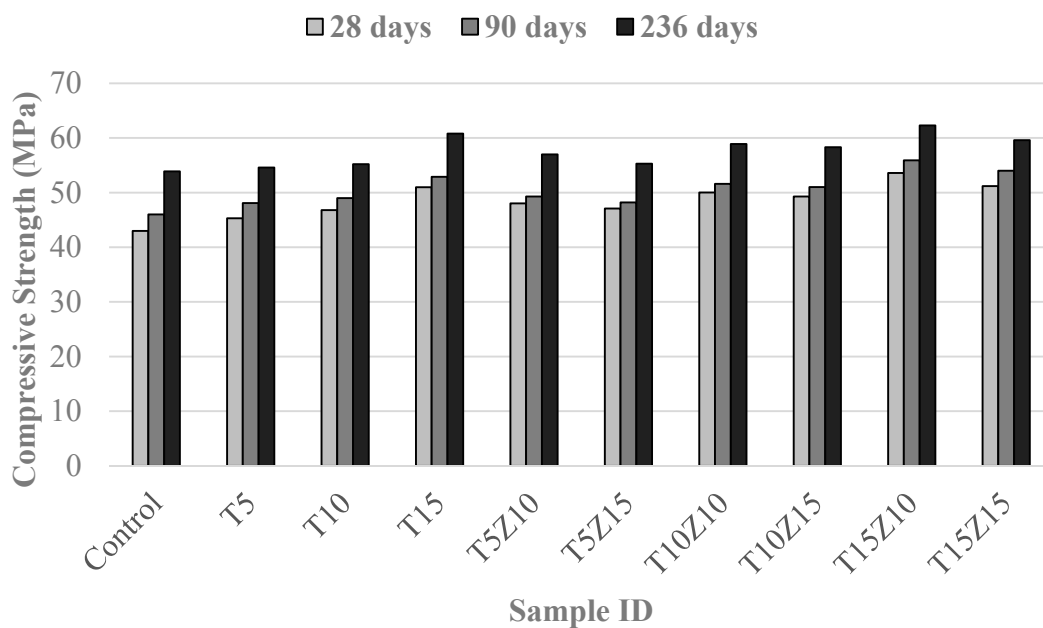
Figure 1. Compressive strengths of the mixtures at different ages.

Figure 2. The fractured face of a sample containing 10% zeolite and 15% tuff after compressive strength test.

Perraki et al. [27] reported that concrete with more siliceous zeolites showed a significant improvement in compressive strength. The zeolite and tuff studied in this paper had a high Si/Al ratio (4.52 in zeolite and 3.47 in tuff) and this might have led to the strength development. Moreover, the development of compressive strength shows that the pozzolanic reaction continued at later ages. A significant strength development can be seen during the period between 90 and 236 days. Some previous studies have reported similar positive effects of tuff and zeolite as cement and aggregate replacement, respectively [28]. Cherrak et al. [29] showed that the replacement of cement by 15% tuff could increase the compressive strength up to 30%. Poon et al. [10] reported that after 28 days of curing, the compressive strength of samples containing zeolite was equivalent to that of the Portland cement paste. Perraki et al. [27] concluded that the addition of 10% zeolite improved compressive strength. Ahmadi et al. [6] also reported improvement in compressive strength, when natural zeolite was used as a partial replacement for cement. The slight decrease in strength observed for specimens with 15% zeolite was probably mainly due to the excessive formation of $Ca(OH)_2$ during the hydration of calcium silicate which was more than the amount of $Ca(OH)_2$ consumed in the pozzolanic reaction.

3.2. Water Absorption

Water absorption results of the concrete samples are presented in Figure 3. It can be seen from the figure that the effect of zeolite on water absorption was somehow different and greater than that of tuff. It is clear to see that the replacement of cement by zeolite could effectively reduce the water absorption, and apparently the higher the replacement percentage was, the lower the water absorption would be.
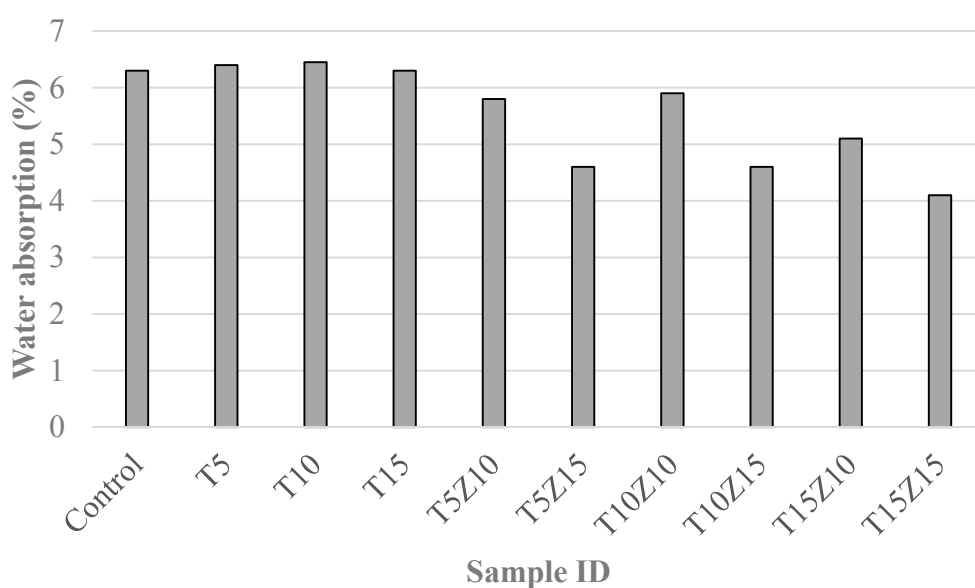

Figure 3. Water absorption of the specimens containing different percentages of zeolite and tuff.

On the contrary, a noticeable change in water absorption was not observed in concrete samples with tuff as sand replacement. For the specimen with 15% tuff, a slight reduction in water absorption was noted. As a consequence, zeolite was considered more effective than tuff to enhance concrete's resistance to permeability. The most remarkable reduction occurred in mixture T15Z15, with a 35% water absorption reduction at the age of 90 days in comparison with the control sample. The results confirmed the beneficial effect of tuff and zeolite on the durability of concrete. The relatively high level of water absorption of samples incorporating tuff was related to the percentage of clay, the void area inside the tuff, the glassy matrix which connected the particles and the voids between these particles, and the compact nature of the tuff [30].

The reduction in water absorption was attributed to the pozzolanic reaction of zeolite developed in the concrete [31]. The rate at which water is absorbed into concrete by capillary suction can provide useful knowledge related to the pore structure, permeation characteristics and durability of the concrete. It can be suggested that the formation of small pores instead of large capillary pores and the blocking of capillary channels which was caused by the formation of additional C-S-H as a result of the pozzolanic reaction refined the pore structure and led to the segmentation of large pores in concrete. This would result in fewer numbers of continuous capillary channels by disconnecting the large pores in concrete. As a result, the flow of water in unsaturated porous concrete was reduced in the presence of zeolite and tuff.

3.3. Chloride Diffusion

Chloride ions can ingress into concrete in different ways including diffusion, capillary suction, migration or a combination of these mechanisms. Diffusion is the movement of dissolved ions due to a concentration gradient in a saturated porous material. This causes a net flow from regions of higher concentration to regions of lower concentration of the diffusing substance [32]. The chloride ion diffusion coefficients of the mixtures are presented in Figure 4. The chloride resistance classifications of concrete such as high, very high and ultra-high, as suggested in the ASTM C1556 Standard [26], are also shown in the figure. Based on the results shown in Figure 4, it can be stated that zeolite as cement replacement could improve the resistance of chloride ingress and the improvement was pronounced when tuff was used to partially replace sand.

As illustrated in Figure 4, the chloride resistance of the control sample was in the high range but the samples with tuff and zeolites showed very high to ultra-high chloride resistance. As indicated, the chloride diffusion coefficient of the control specimen was 8×10^{-12} m^2/s, which was reduced by up to 55% when 15% tuff and 10% zeolite were used. Thus, it is identified that the resistance of the specimens to chloride diffusion was significantly enhanced by the presence of tuff and zeolite.

In this experiment, specimens were made, cured and examined in identical conditions so that the rate of ingress of chloride into the concrete was highly related to the pore structure of the concrete, which was affected by different factors including the ingredients, particle packing, and the degree of reaction of the cementitious materials. This was also influenced by the inclusion of supplementary cementing materials which serve to subdivide the pore structure [33]. The additional C-S-H gel produced in the presence of tuff and zeolite, as shown by Equation (5) is the reason for the micro-structure improvement in hardened concrete. The reactive SiO_2 and Al_2O_3 in concrete can convert $Ca(OH)_2$ into C-S-H gel and aluminates and eventually improve the micro-structure of concrete.

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4{}^{2-} + 2H_2O \rightarrow CaH_2SiO_4 + 2H_2O. \tag{5}$$
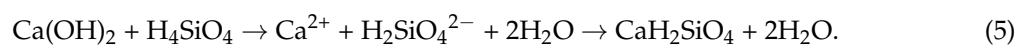
It can be seen that the chloride resistance results are in good agreement with the water absorption results, and it is apparent that the high resistance to water and chloride penetration may be related to the reduced porosity of concrete containing zeolite and stuff. It is believed that the addition of 15% zeolite and 15% tuff could reduce the porosity substantially. However, the effect of tuff on permeability was found to be higher when compared with the effect of zeolite. When these two materials were used together, a dense structure with improved resistance against chloride diffusion was observed. Previous work has also observed similar effect of zeolite on reducing the chloride diffusion. Ahmadi et al. [9] reported that up to 20% natural zeolite reduced chloride diffusion coefficient of concrete. Chan et al. [8] concluded that even at a low water-to-binder ratio (0.28), the replacement of cement with zeolite from 5% to 30% reduced the chloride diffusion of concrete. The use of zeolite in self-consolidating high performance concrete also caused a decrease in chloride diffusion due to the improvement of micro structure [34].
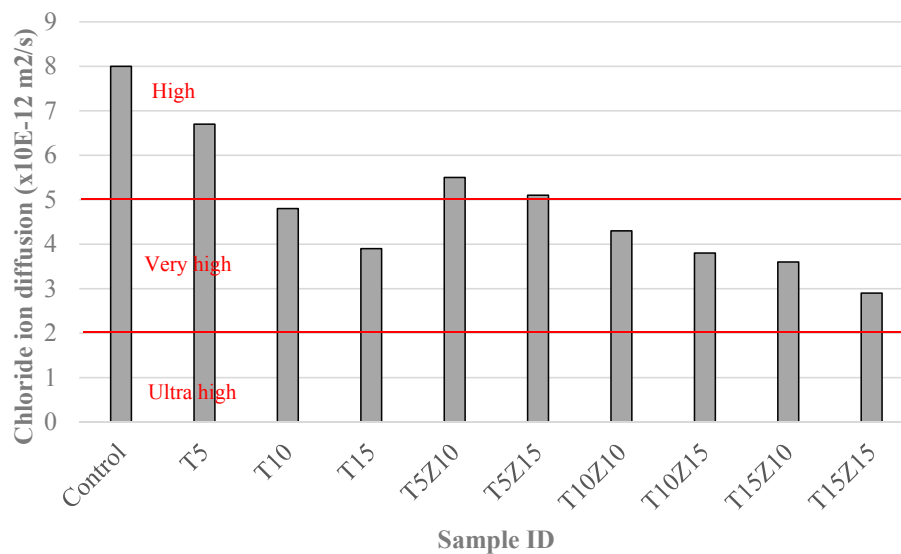
Figure 4. Chloride ion diffusion coefficients of concretes containing tuff and zeolite as compared to the chloride resistance classifications of ASTM 1556.

3.4. Resistance to Acid Attacks

3.4.1. Resistance to Sulphuric Acid

Figures 5–7 show the physical appearance of the typical concrete samples before and after exposure to an acid solution. It can be seen from Figure 7 that the surface of samples suffered from significant erosion by the acid attack. When sulphuric acid reacted with the hydration products, the dissolution of hydrated composites and hydrogen ions occurred. The speed of this action is dependent on the pore structure, porosity, sulphuric acid concentration and pH of the solution [35]. As mentioned before, the concentration of the acid solution was kept constant at 5%. According to Figure 7, the specimens experienced the most aggressive conditions right after they were immersed in the acid solution. Figure 8 presents the mass loss that occurred in the concrete specimens after 180 days of immersion in sulphuric acid (H_2SO_4) solution. The results indicated that tuff did not have a positive impact on sulphuric acid resistance of concrete samples. All the specimens were found to have increased damage when tuff was used in the concrete. The deterioration of samples was mainly due to the decomposition of hydration products, in which the reaction of acid with lime increased the amount of highly soluble calcium by-products. A similar reduction in chemical resistance was also observed by other researchers [29].

Another reason that made specimens with tuff more vulnerable to acid attack was that sand without pozzolanic function was replaced by a material with pozzolanic properties (tuff with high silica content). In this case, the specimens were made with more paste volume which was less resistant to the acid attack. However, the addition of zeolite seemed to alleviate the undesirable impacts of the addition of tuff in concrete specimens, since it contained 2.24% calcium in comparison with cement that contained 63.75% calcium. Consequently, addition of zeolite as a cement replacement is highly recommended in acidic environments, whereas the incorporation of tuff alone as a sand replacement in acidic environments does not appear to be beneficial.

The mass loss in the control sample was 3.3% and the mass reduction of T5, T10 and T15 were 54%, 88% and 106% higher than the control sample. The mass loss in the concrete can be explained by the following reactions of sulphuric acid in concrete:

1. Sulphuric acid reacted with the calcium hydroxide and converted it to calcium sulphate

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O. \tag{6}$$
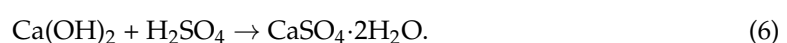
Calcium sulphate could leach out of concrete or reacted with calcium aluminate.

2. The calcium sulphate from the previous reaction reacted with calcium aluminate to form ettringite that could cause cracking and expansion.

$$3CaSO_4 + 3CaO \cdot Al_2O_3 \cdot 6H_2O + 25H_2O \rightarrow 3CaO \cdot Al_2O_33CaSO_4 + 31H_2O. \tag{7}$$
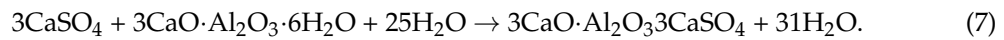
3. The calcium silicate hydrate reacted with sulphuric acid and the product was the silica gel.

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O + Si(OH)_4. \tag{8}$$
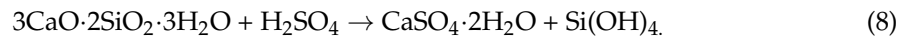
To study the effect of sulphuric acid on strength of concrete samples, the compressive strength of concrete samples was measured after 236 days of immersion. The compressive strength test results are given in Table 4. The strength reduction varied between 9.71% and 21.48%, however the strength reduction of control concrete sample was merely 5.01%. This reduction of strength can be attributed to the reaction of sulphuric acid with $Ca(OH)_2$. The amount of $Ca(OH)_2$ was not sufficient for pozzolanic reaction, and the concrete samples with tuff lost some parts of the C-S-H gel. The reduction in compressive strength was due to the following reasons:

1. Depth of reaction (DR): it is the depth which contains the weakened depth of the concrete specimen but is still attached to the concrete. In this weakened layer, components such as alkalis, $Ca(OH)_2$ (at the beginning) and, later, C-S-H phases, dissolved, which formed new phases, such as calcium sulphates.
2. Depth of erosion (DE): it is the depth in which the paste can be totally extracted manually or by using a wire brush. The depth of erosion consists of the layer of the specimen from which the hardened cement paste is totally extracted from concrete. The DE was quantified after 236 days of immersion by measuring the dimensions of the samples. The results of average DE are presented in Figure 8. The results showed that concrete with tuff was more vulnerable to acid attack in comparison with both the control sample and the samples containing zeolite. Since tuff was used as a substitution of sand, the samples with tuff incorporated the same cement volume in addition to 5%, 10% and 15% tuff which could also work as pozzolans compared to the control sample. As a result, the chemical reaction of cement and tuff with sulphuric acid solution produced a thicker gel-like white cover. This gel-like cover was soluble and soft and could be removed manually.

On the other hand, the presence of zeolite as a cement replacement could rather compensate for the effects of tuff in concrete. The presence of zeolite could significantly reduce the calcium-containing compounds in the cement paste which led to less calcium hydroxide.

Figure 5. Samples immersed in acid solution.

Figure 6. Physical appearance of typical samples in 5% sulphuric acid solution.

Figure 7. Physical appearance of typical samples after immersion in 5% sulphuric acid solution.
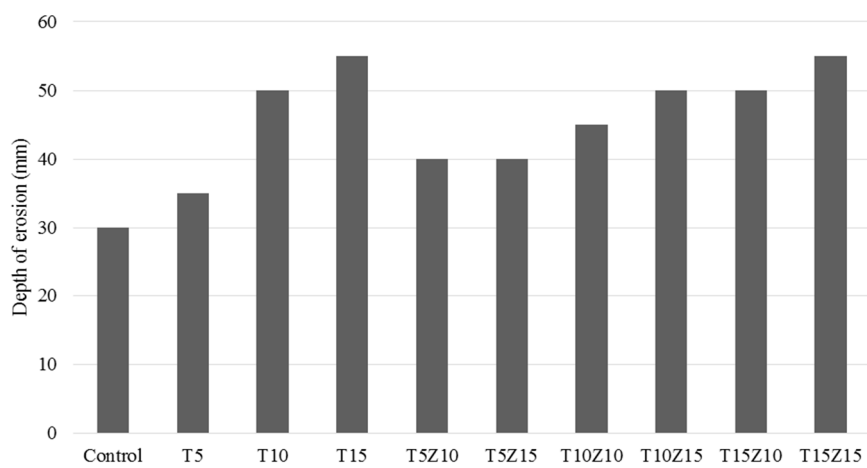

Figure 8. Depth of erosion.

Table 4. Compressive strength after 236 days immersion in acid.

Mix ID	Compressive Strength (MPa)		Strength Reduction in Acid (%)
	28 Days in Water + 28 Days in Lab Condition + 180 Days in Acid Exposure	236 Days in Water	
Control	51.2	53.9	5.01
T5	49.3	54.6	9.7
T10	50.1	55.2	9.2
T15	51.2	60.8	15.7
T5Z10	48.3	57	15.2
T5Z15	44.1	55.3	20.2
T10Z10	51.2	58.9	13.07
T10Z15	49.3	58.3	15.4
T15Z10	51.3	62.3	17.6
T15Z15	46.8	59.6	21.4

3.4.2. Resistance to Hydrochloric Acid

The mass loss values of the specimens due to hydrochloric acid attack are given in Figure 9. Hydrochloric acid damages the concrete through a dissolution process. The mass loss of the concrete specimens with different tuff and zeolite percentages after 180 days of exposure to hydrochloric acid were in the range of 3.28% to 4.8%. The highest mass loss was 4.8% and it was observed in the concrete with 15% zeolite and 15% tuff.
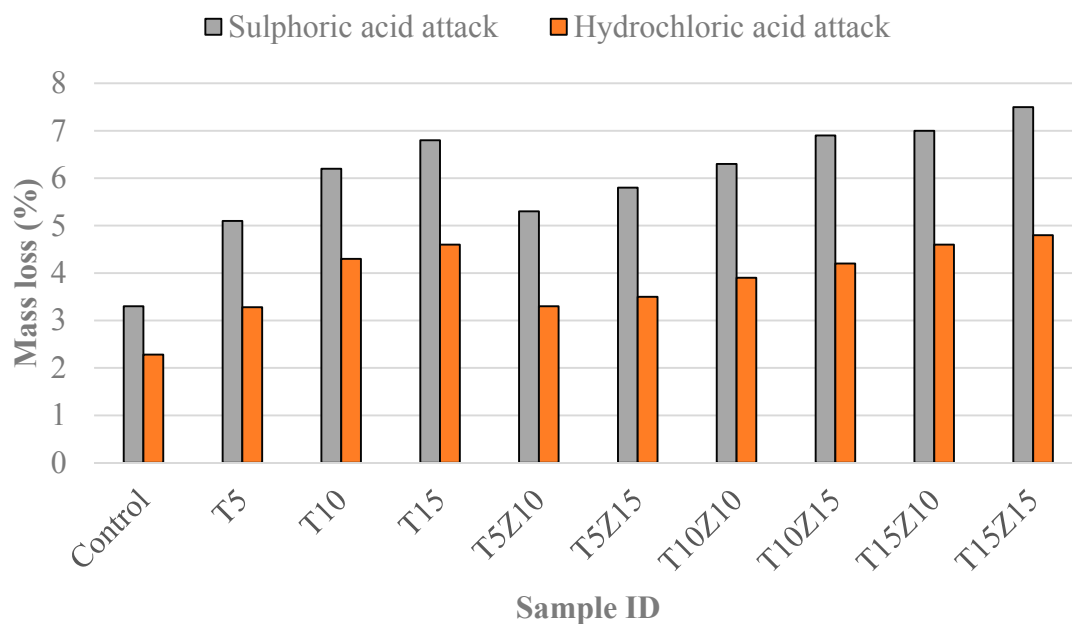

Figure 9. Mass loss by sulphuric and hydrochloric acid attack of specimens containing different percentages of zeolite and tuff.

The mass loss percentage in the control sample was 2.28% and the specimens with 5%, 10% and 15% tuff experienced 56%, 91% and 102% higher mass loss in comparison with control sample. Slightly less sensitive to HCl aggression were the mixes of T5, T5Z10, T5Z15 and T10Z10, which seemed qualified to be more resistant to acidic aggression. It is clear that the specimens immersed in hydrochloric acid showed similar degradation in terms of the mass reduction percentage. The chemical reaction of hydrochloride acid with lime is:

$$2HCL + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O \tag{9}$$
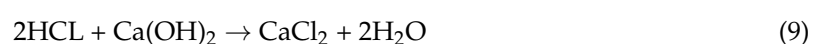
Calcium chloride (CaCl$_2$) is a highly soluble and harmful salt that can easily leach out of the concrete and therefore results in deterioration of concrete. Cherrak et al. [29] reported that although the concrete specimens immersed in hydrochloric acid and sulphuric acid showed the same degradation regarding the aggregates, the leaching out of concrete happened from less depths when immersed in hydrochloride acid.

4. Conclusions

Based on the results, the following conclusions are drawn:

1. Concrete containing 15% tuff and 10% zeolite showed the highest compressive strength.
2. Replacement of cement by zeolite substantially decreased the water absorption. However, in concrete samples with tuff as sand replacement, considerable absorption was not observed.
3. The chloride diffusion coefficient of the control specimen diminished by up to 55% in T15Z10 sample. Thus, it is identified that the chloride resistance of the specimens was significantly enhanced by the use of tuff and zeolite.
4. The compressive strength reduction of concrete samples in sulphuric acid after 236 days of immersion varied between 9.2% and 15.7% in tuff-included samples and also 13.07% and 21.4% in tuff- and zeolite-included samples, however the strength reduction of plain concrete sample was 5.01%.
5. The highest mass loss of 4.8% was recorded for specimen 15T15Z after 180 days of exposure to hydrochloric acid.

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