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Quantifying the Effect of Ammonium Nitrate Attack on Mechanical and Physical Properties of Cement Mortars

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Authors' contributions

This work was carried out in collaboration between all authors. Author MA designed the study, developed the methodology and contributed in the literature review and analysis of the results. Author MA conducted a comprehensive literature review and contributed in analysis of the results. Author TS executed the experimental program and helped in literature review and analysis of the results. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2015/16824 <u>Editor(s):</u> (1) Prinya Chindaprasirt, Khon Kaen University, Thailand. <u>Reviewers:</u> (1) Anonymous, University of Science and Technology Houari Boumediene, Algeria. (2) Anonymous, CSIR- Building and Road Research Institute, Ghana. (3) Brajadulal Chattopadhyay, Department of Physics, Jadavpur University, Kolkata, India. (4) Anonymous, University of Campinas, Campinas, Brazil. (5) Mohamed Ismail, Hanyang University, South Korea. Complete Peer review History: <u>http://www.sciencedomain.org/review-history.php?iid=1126&id=22&aid=9056</u>

Short Research Article

Received 15th February 2015 Accepted 9th April 2015 Published 30th April 2015

ABSTRACT

The purpose of the current study is to quantify the effect of ammonium nitrate attack on the mechanical and physical properties of cement mortars. After 28 days of curing, the mortar specimens were immersed in ammonium nitrate solutions with 5%, 20% and 50% concentrations. The specimens were then tested after 10, 20, 40 and 60 days. The results showed that at 5% and 20% concentrations, the compressive strength loss of cement mortar after 60 days of exposure was 23% and 43%, respectively. For 50% concentration, the loss in compressive strength reached 55% at 60 days of exposure. At 50% and 20% concentrations, the porosity of cement mortar increased by 10.9% and 3.9% after 60 days of exposure, respectively. The loss in the bulk density at 5% and 20% concentrations of ammonium nitrate solution after 60 days of exposure was about 3% and 6%, respectively. The increase in porosity and the losses in compressive strength and bulk density could be overcome by using high compressive strength concrete, pozzolanic additives and low water-cement ratio.

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Keywords: Cement mortar; concrete; compressive strength; porosity; strength loss.

1. INTRODUCTION

Concrete material is the most commonly used building materials all over the world. Concrete elements are utilized in various structural applications as sub-structural and superstructural elements [1,2]. This wide use of concrete elements comes from the fact that concrete has adequate durability, compressive strength, impermeability, abrasion resistance, and resistance to environmental attacks [2]. However, concrete mix is made of cement which, as a chemical compound, is susceptible to attack by aggressive environments.

These aggressive environments comprise soft waters, sea waters, ground waters, industrial environments, wastewaters and polluted environments [1]. There are many parameters affecting the susceptibility of concrete to such harmful environments; among them are porosity, density and permeability at the time of its exposure to aggressive agents [2].

Such aggressive environments promote several harmful chemical and biological reactions with cementitious materials of the concrete. These reactions develop a degradation process of the concrete, resulting in disintegration of its microstructure relations. The continuation of this process will weaken the concrete and decreases its durability. In addition, reinforcement of concrete is continuously under corrosion process, leading eventually to total or at least major damages to the structures [1]. Therefore, the deep understanding of such degradation process plays a significant role to obtain concrete which would has enough capability to withstand these aggressive environments and enhance the durability of concrete structures.

Among these aggressive attacks which can quickly degrade cementitious materials available in concrete is ammonium nitrate salts. Ammonium nitrate [3], which is commonly used as a fertilizer, has a severe degrading and corrosive influence on concrete elements, such as in ammonium nitrate manufacturing factories and storage tanks. It leads to degradation of the concrete cementitious materials according to the following reactions:

$$Ca(OH)_2 + 2NH_4NO_3 \rightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O$$
(1)

 $\begin{array}{l} (CaO)_{3}(SiO_{2})_{2}(H_{2}O)_{8} + 4NH_{4}NO_{3} \rightarrow 2Ca(NO_{3})_{2} \\ + 4NH_{3} + (CaO)(SiO_{2})_{2}(H_{2}O)_{6} + 4H_{2}O \end{array} \tag{2}$

Chemical attack by ammonium nitrate ions produces calcium nitrate $Ca(NO_3)_2$ and ammonia NH₃ [1,3]. These newly produced compounds readily dissolve in water, causing dissolution of calcium hydroxide (Ca(OH)₂). In addition, this process will progressively develop decalcification of calcium silicate hydrate (C-S-H) of the hardened concrete [4,5]. This calcium leaching process causes deterioration of the strength and durability properties of the hardened concrete [2,6,7].

Wong et al. [2] investigated the durability of concrete when exposed to 20% concentration solution of ammonium nitrate. They studied the effect on water absorption, volume of permeable voids, compressive strength and pH value. Their results revealed that the higher compressive strength concrete performs better and it is less susceptible to damage than the lower compressive strength concrete.

Bellego et al. [8] investigated the loss of mechanical properties due to calcium leaching caused by 480g/L ammonium nitrate NH_4NO_3 solution, as an aggressive environment. They tested mortar beams with three different sizes after immersion for different periods of time in the aggressive solution. Their results showed a loss of apparent stiffness, a reduction in ultimate load capacity and a reduction in fracture energy when leaching takes place.

Agostini et al. [7] conducted an experimental study on two thin walled hollow cylinders of mortar with two different initial porosities. These two mortars were degraded by using ammonium nitrate solution. The leaching effects were measured by obtaining the variations in mechanical and hydraulic properties. There was an increase of permeability magnitude and 85% loss in compressive strength and elastic modulus in both mortars.

Nguyen et al. [9] conducted an experimental program to obtain the chemo-mechanical behavior on calcium leached concrete. They highlighted the strong coupling between the calcium leaching and the mechanical behavior; as leaching proceeds, a loss of stiffness and of compressive strength were noticed.

Segura et al. [10] presented the results of microstructural characterization of cement mortars made with three water-cement ratios and five cement types and degraded by immersion in ammonium nitrate solutions. Based on these results, they proposed two parametric equations to estimate the decalcification process, kinetics and degradation depth using basic parameters, such as open porosity, cementitious matrix volume fraction and initial CaO content.

The current study aims at quantifying the effect of ammonium nitrate at three different concentration solutions on mechanical and physical properties of cement mortars. Concentrations of ammonium nitrate ranging between 5% and 50% were used to represent the concrete elements in chemical factories and silos. The mechanical and physical properties which were conducted in this study comprise compressive strength, porosity and bulk density tests.

2. MATERIALS AND METHODS

2.1 Materials Properties

2.1.1 Cement

In this research Al-Areesh Ordinary Portland cement CEM I 52.5 N produced in Egypt was used. The cement satisfied the requirements of ASTM C150 [11] specifications. The physical and mechanical properties of the cementused are summarized in Table 1. The Chemical and mineralogical properties of the cement are given in Table 2.

Table 1. Physical and mechanical properties of cement CEMI

Test type		Results
Setting time (Vicat test)	Initial	126 (86)
hr:min	Final	155(115)
Mortar compressive	3 Days	
strength (MPa)	7 Days	
	28 Days	57
Fineness (cm ² /g)		3020
Normal consistency (%)		27

2.1.2 Fine aggregate

Local dune sand was utilized as fine aggregate. The specific gravity and water absorption of the fine aggregates were 2.6 and 0.57% respectively. The maximum sieve size for the fine aggregate was 600 μ m. The grading of the fine aggregate is given in Table 3. These tests were done according to ASTM C128 [12] and ASTM C136 [13].

Table 2. Chemical and mineralogical
properties of the cement CEM I

Chemical composition (%)	Cement CEM I
CaO	63.5
SiO ₂	19.9
Al ₂ O ₃	4.9
Fe ₂ O ₃	2.3
MgO	1.7
SÕ ₃	2.9
Na ₂ O	0.4
K ₂ O	0.8
Compound Composition (%)	
C₃S	51.5
C ₂ S	25.7
C ₃ A	11.3
C ₄ AF	8.1

Table 3. Grading of the fine aggregate

Sieve size (mm)	Cumulative percentage passage (%)
0.60	100
0.30	61
0.15	2.8
0.075	1.3

2.1.3 Water

Distilled water without any salts or chemicals was used in mixing, curing and preparing different aggressive solutions for immersion stage. The water was supplied by the Soil and Material Lab of the Islamic University of Gaza.

2.2 Preparation of Ammonium Nitrate Solutions

Ammonium nitrate solutions with 5% (50 g/L), 20% (200 g/L) and 50% (500 g/L) concentrations were applied to investigate their effects on the cement mortars. The specimens were arranged on layers in basins by using plastic meshes, in order to ensure that all specimen's surfaces were in direct contact with ammonium nitrate solutions. The basins of ammonium nitrate solutions were covered by plastic lids to prevent the evaporation of the ammonia gas produced by reaction of ammonium nitrate and the hydrated cement.

2.3 Mix Proportions and Specimens Preparation

The prepared specimens in this study were based on the requirements of ASTM C109 [14]. The water-cement (w/c) ratio was 0.45 for all specimens and the cement-sand ratio was set at 0.4. Table 4 presents the mix proportions of cement mortar.

Table 4. Mix proportions of cement mortar

Components	Mortar
Fine aggregate (kg/m ³)	1450
Cement (kg/m ³)	580
Water (kg/m ³)	261
(w/c) ratio	0.45

Test specimens were prepared by placing the cement mortar into 5 cm \times 5 cm \times 5 cm molds. After 24 hours, the specimens were stripped and cured in a water tank at room temperature for 28 days, as seen in Fig. 1. Afterwards, specimens were immersed in ammonium nitrate solutions for 10, 20, 40 and 60 days before testing. The choice of immersion periods was complied with Gaitero et al. [15]. As soon as the suggested immersion period was reached, the specimens were moved into a distilled water tank for 10 days before testing. Agostini et al. [7] indicated that periods after 10 days did not reveal significant weight variations.

Each series of specimens were finally dried in an oven at a moderate temperature of 60°C for at least 48 hours. One reason for such drying process was to carry out the porosity and loss of mass measurements [7]. The other reason was due to the fact that higher temperatures increase the rate of hydration which lead to micro-cracking induced by shrinkage and differential strains

between cement paste and aggregates [7]. Therefore, the dried state was considered as a reference to compare intact and degraded material. The mean value of the three specimens was taken for each test result.

2.4 Porosity Test

Porosity was obtained by calculating the difference between saturated and dried specimen weights. In order to calculate the porosity ratio (%), the weight of leached specimens was measured after soaking in water tank for 10 days (W_1). The weight of specimens (W_2) was also measured after drying in an oven for 48 hours at 60°C (see Figs. 2 and 3). The applied measurement of porosity was complied with that followed by Agostini et al. [7]. Therefore,

% Porosity =
$$\left[\frac{W_1 - W_2}{W_2}\right] \times 100$$
 (3)

2.5 Bulk Density Test

Bulk density is the weight per unit volume. The weight of specimens was measured after drying in an oven at 60°C for 48 hours and specimen volume was calculated from specimen dimension measurements.

2.6 Compressive Strength Test

Compressive strength tests were performed on the 5 cm \times 5 cm \times 5 cm cement mortar cubes in accordance with ASTM C109 [14] at 10, 20, 40 and 60 days of immersion in ammonium nitrate solutions. The specimens were placed on a testing machine with a rate of 0.5 kN per second to execute the uniaxial compression test.



Fig. 1. Curing of specimens in water tanks

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Fig. 2. Drying of specimens in an oven



Fig. 3. Weight of specimens

The compressive strength of the specimen (σ_{comp}) was calculated by dividing the maximum load carried by the cube specimen during the test (P) by the cross sectional area of the specimen (A) as shown in Eq. (4).

$$\sigma_{\rm comp} = \frac{P}{A} \tag{4}$$

3. RESULTS AND DISCUSSION

3.1 Compressive Strength

The results of the compressive strength of the cement mortars stored in distilled water and those obtained from the immersion in 5%, 20% and 50% ammonium nitrate solutions at different ages of 10, 20, 40 and 60 days are presented in Fig. 4. Then, the loss in compressive strength of

cement mortars was calculated by Eq. (5) as shownin Fig. 5.

Loss in compressive strength (%) =

$$\left[\frac{f_{c28} - f_c}{f_{c28}}\right] \times 100$$
(5)

Where f_c is the compressive strength of the cement mortars immersed in the aggressive solutions and f_{c28} is the compressive strength at 28 days of curing in distilled water. f_{c28} was used as the reference compressive strength.

Figs. 4 and 5 revealed that at 60 days storage in distilled water, the compressive strength was increased from 47 MPa to 55 MPa. This indicates that the compressive strength was17% higher than its initial compressive strength.

It was also observed that soaking the mortar cubes in different concentration of ammonium nitrate solutions adversely influenced the compressive strength of cement mortars. At 5% concentration of ammonium nitrate. the compressive strength of mortar specimens was reduced from 47 MPa to 36 MPa at 60 days of exposure, which means a 23% loss in compressive strength. At 20% concentration of ammonium nitrate, the compressive strength was decreased from 47 MPato 38 MPa at 20 days of exposure, that was a loss of 19% in compressive strength. This reduction reached a lower value of 27 MPa at 60 days of exposure, resulting in total reduction of 43% compared with reference ones.

The compressive strength of the cement mortars immersed in 50% ammonium nitrate solution was decreased to 30 MPa and 55 MPa at 20 and 60 days of exposure, respectively. This indicates that the loss in compressive strength at 20 days and 60 days of exposure reached 21% and 55%, respectively.

The results revealed that as the ammonium nitrate concentration increased, the loss in compressive strength significantly increased at all exposure periods. Based on the findings of Wong et al. [2], Nguyen et al. [9] and Agostini et al. [7], the loss in compressive strength could be attributed to the removal of calcium hydroxide and the progressive decalcification of calcium silicate hydrate of the hardened mortars. They also found out that the aggressive ammonium nitrate attack produced a readily soluble calcium nitrate salt and ammonia. This causes development of voids or pores within cement

mortar. These voids weaken the compressive strength of cement mortar.

Wong et al. [2] showed that the compressive strength decreased when the concrete was attacked by ammonium nitrate solution. They indicated a loss in compressive strength of 24.91% for concrete specimens at 56 days of exposure, while this reduction in strength reached 47.44% at 90 days of exposure.

3.2 Porosity

The measurements of porosity of cement mortars stored in distilled water and in 5%, 20% and 50% ammonium nitrate solutions at different ages of 10, 20, 40 and 60 days are shown in Fig. 6.

It was observed that the porosity of cement was considerably increased mortar after in different concentrations immersion of ammonium nitrate solutions. At 5% concentration, the porosity of cement mortars increased from 5.1% to 6.4% at 60 days of exposure. For the 20% concentration, the porosity increased by 1.4% and 3.9% at 20 and 60 days of exposure, respectively. The porosity of the cement mortars at 50% concentration of ammonium nitrate increased from 5.1% to 9.5% and 16% at 20 and 60 days of exposure, respectively. This indicates that there was a considerable increase in porosity of the cement mortar at high concentrations of ammonium nitrate and increasing time of exposure. Agostini et al. [7] found that the porosity increased from 11% to 14% at 16 days of exposure of cement mortars in ammonium nitrate solutions.



Fig. 4. Compressive strength of cement mortars immersed in distilled water and in different concentrations of ammonium nitrate at different time of immersion

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Fig. 5. Loss in compressive strength of cement mortars immersed in 5%, 20% and 50% concentrations of ammonium nitrate at different time of immersion



Fig. 6. Porosity of cement mortars immersed in distilled water and in different concentrations of ammonium nitrate at different time of immersion

The increase of cement mortar porosity due to immersion in ammonium nitrate could be referred to the removal of calcium hydroxide and the progressive decalcification of calcium silicate hydrate compounds, as shown in Eqs. (1) and (2). This removal process causes more voids to form within mortar, increasing the permeability of the material and eventually decreasing the mortar strength and its durability.

3.3 Bulk Density

Fig. 7 indicated that for different concentrations of ammonium nitrate solutions, the bulk density of cement mortar is moderately affected. For 5% concentration of ammonium nitrate, the bulk density decreased from 2.18 g/cm³ to 2.12 g/cm³, while the bulk density decreased from 2.18 g/cm³ to 2.04 g/cm³ for 20% concentration at 60 days of immersion. The loss in bulk density of cement mortars immersed in 50% ammonium nitrate solution for 60 days was about 9%. Based on the obtained results, it can be explained that the bulk density moderately decreased when the mortar specimens was immersed in ammonium nitrate solutions. Agostini et al. [7] found that the bulk density of the cement mortars decreased from 1.88 g/cm³ to 1.59 g/cm³ at 16 days of immersion in ammonium nitrate.

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Fig. 7. Bulk density of cement mortars immersed in distilled water and in different concentrations of ammonium nitrate at different time of immersion

The reduction in bulk density couldalso be attributed to the same mechanism of calcium hydroxide removal and decalcification of calcium silicate hydrate compounds. This process causes slight to moderate loss of cement mortar constituents, therefore reduction in bulk density.

4. CONCLUSIONS

Based on the experimental results, the following conclusions were made:

- 1) There was a prominent influence of ammonium nitrate concentrations on the compressive strength of cement mortar. The compressive strength of cement mortar decreased when it was exposed to ammonium nitrate solutions. As the of ammonium concentration nitrate solutions and time of exposure increases, the loss in compressive strength significantly increases.
- The porosity of cement mortar increased when it was exposed to ammonium nitrate solutions. The porosity of cement mortar increases as the concentration of ammonium nitrate and time of exposure increases.
- The bulk density of cement mortar decreased when it was exposed to ammonium nitrate solutions. The loss in bulk density increases as the concentration of ammonium nitrate solutions increases. As the exposure period to ammonium

nitrate solutions increases, the reduction in bulk density of cement mortar increases.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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