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Effects of Aggressive Ammonium Nitrate on Durability Properties of Concrete using Sandstone and Granite Aggregates

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***Abstract*—**The storage of chemical fertilizers in concrete building often leads to durability problems due to chemical attack. The damage of concrete is mostly caused by certain ammonium salts. The main purpose of the research is to investigate the durability properties of concrete being exposed to ammonium nitrate solution. In this investigation, experiments are conducted on concrete type G50 and G60. The leaching process is achieved by the use of 20% concentration solution of ammonium nitrate. The durability properties investigated are water absorption, volume of permeable voids, and sorptivity. Compressive strength, pH value, and degradation depth are measured after a certain period of leaching. A decrease in compressive strength and an increase in porosity are found through the conducted experiments. Apart from that, the experimental data shows that pH value decreases with increased leaching time while the degradation depth of concrete increases with leaching time. By comparing concrete type G50 and G60, concrete type G60 is more resistant to ammonium nitrate attack.

***Keywords*—**Normal weight concrete durability, Aggressive Ammonium Nitrate Solution, G50 & G60 concretes; Chemical attack.

I. Introduction

CONCRETE is an economical construction material which is employed in a wide variety of applications on the ground, underground, and under sea level. It is used in foundations, pavements, storage tanks, piles, buildings, dams, and other structures. Durability, compressive strength, impermeability, abrasion resistance, and resistance to environment attacks are important properties of concrete. Durability is the capacity of concrete to resist deterioration from heating and cooling, freezing and thawing, and action by chemicals such as fertilizers. Concrete that is durable requires the integration of design, materials, and construction. It depends on the materials used, full compaction, and adequate curing [1]. Concrete exposed to aggressive environment lead to deterioration of concrete. Chemical fertilizer plant is considered as aggressive environment. Different types of fertilizers will attack concrete and heavily damage it. Factors that affect the susceptibility of concrete to damage include chemical composition of its ingredients and physical factors such as porosity, density and permeability at the time of its exposure to corrosive agents. However, the maximum damage of concrete is reported to be caused by ammonium salt.

Ammonium nitrate causes dissolution of cement-based materials through the reaction between ammonium nitrate and calcium hydroxide in the cement paste. The reaction is expressed in (1):

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

The reaction between ammonium nitrate and concrete was reported as potentially aggressive. Due to the removal of calcium hydroxide, the hardened cement paste will be decalcified causing the pH value to decrease [2]. The reaction yields calcium nitrate and ammonia, both of which are easily water-soluble. Subsequently, an expansive calcium nitro-aluminate is formed by reaction between calcium nitrate and hydrated aluminates from the cement paste [3]. Lea [4] reported that this compound forms “climbing salts” by the transportation of water from humid to dry surface. The concrete is weakened through the leaching of lime in cement paste. This eventually leads to cracking on the concrete surface. The deterioration of concrete reduces the effectiveness of concrete as protective cover for steel reinforcement. The steel reinforcement will be corroded, leading to spallation of concrete [2].

The durability of concrete subjected to aggressive environments is affected by transport properties, which are influenced by the pore system [5]. Major factor influencing the durability is the permeability of the concrete. Permeability allows the ingress of oxygen, carbon dioxide, water, and other deleterious substances into the concrete. Permeability should be kept to the minimum level by using sufficient cement contents, low water/cement (w/c) ratio, adequate compaction and sufficient hydration of the cement through appropriate curing methods [6].

II. Experimental Details

A. Materials for Concrete Mixtures

Cement

The cement used conforms to the requirements set under ASTM C-150 [7], Type 1 Ordinary Portland Cement.

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Coarse Aggregate

Coarse aggregates composed of granite and crushed sandstone within the range of 10 mm to 14 mm. Physical properties of the coarse aggregates are given in the TABLE I.

Fine Aggregates

The size of river sand ranged from 75 µm to 4.75 mm. It was dried in a shielded place for a week. Then, it was sieved to find the fineness modulus. Physical properties of the fine aggregates are given in TABLE I.

Fly Ash

Fly ash used in this research to improve the workability and ultimate strength of concrete. It also used to improve resistance to sulphate attack and reduce permeability.

Silica Fume

Silica fume also added in concrete to produce high strength, dense and durable concrete.

Superplasticizer

Superplasticizer was added to increase the strength of concrete. It is a water-reducing admixture which facilitates work with concrete of low w/c ratio. It is also used to eliminate segregation of concrete and allow good dispersion of cement particles in water, accelerating the rate of hydration [8].

TABLE I
PROPERTIES OF COARSE AND FINE AGGREGATES

Characteristics	Granite	Crushed Sandstone	River Sand
Size Range	10mm to 14mm	10mm	75µm to 4.75mm
Fineness Modulus	-	-	2.18
Moisture Content	0%	1.27%	0%
Specific Gravity	2.80	2.62	2.74

B. Concrete Sample Preparations

The mix proportions were prepared as in TABLE II. The mixer was pre-damped with water. Half of the coarse aggregate was added and then followed by fine aggregate and finally the remaining coarse aggregate by spreading them evenly over the pan and the mixer was operated for 30 second. After that, half of the water is mixed for 1 minute. The cement, silica fume and fly ash were added in an even layer over the aggregate. The mixture was then mixed for 1 minute. Finally, the remaining water and superplasticizer were added and mixed uniformly to produce concrete grade 50 and 60. The concrete was then placed in the cube mould in three layers and each layer was compacted by using vibrating table. The concrete specimens were left undisturbed for 24 hours and then demoulded. The specimens were cured for 3, 7, 28, 56, and 90 days respectively in the water tank for normal curing method.

After 28 days curing of specimens, some of the specimens were partially immersed in ammonium nitrate solution with concentration of 20% until 56 day and 90 day (include curing age) before testing. The container was closed by lid to prevent the ammonia gas produced by reaction of ammonium nitrate and calcium hydroxide to be evaporated in the air. To determine the durability properties, tests conducted were water absorption, volume of permeable voids (VPV) and sorptivity test. Other tests such as compressive strength test, pH measurement and degradation depth measurement were also determined.

TABLE II
MIX PROPORTION OF CONCRETE TYPE G50 AND G60

Concrete Type	G50	G60
Cement (kg/m^3)	500	440
Fly Ash (kg/m^3)	-	71.5
Silica Fume (kg/m^3)	30	38.5
River Sand (kg/m^3)	500	312
Crushed Sandstone (kg/m^3)	-	220
Granite (kg/m^3)	1140	1056
Water (kg/m^3)	186	165
S.P (%)	1.67	1.67

III. TEST RESULTS AND DISCUSSIONS

A. Compressive Strength Test

The testing procedure is complied with BS 1881: Part 116: 1983 [9]. The results for the compressive strength test are shown in Fig. 1. The compressive strength decreased when the concrete was treated with ammonium nitrate solution. For concrete type G50, the strength decreased to 42.71 N/mm^2 at the age of 56 days whereby there was a difference of 24.91% in strength compared to the concrete cured in water at the same age. It continued to decrease until 30.88 N/mm^2 at the age of 90 days, leading to a difference of 47.44% compared to those immersed in water. For concrete type G60 treated with ammonium nitrate solution, the strength decreased from 51.11 N/mm^2 at the age of 56 days to 38.28 N/mm^2 at the age of 90 days. The percentage of difference in strength between concrete treated with ammonium nitrate solution and water at the age of 56 days was about 22.48% while for concrete at the age of 90 days, the difference in strength was 42.06%. The loss of strength for concrete type G60 was less than concrete type G50 after leaching by ammonium nitrate solution, indicating that concrete type G50 was more susceptible to damages done by ammonium nitrate solution compared to concrete type G60.

Based on the research of Carde and Francois [10], the loss of strength was essentially due to the removal of calcium hydroxide during the leaching process by ammonium nitrate solution. Calcium hydroxide is the hydration product which replaces the space occupied by cement and water during hydration process. The calcium hydroxide reacts with ammonium nitrate yielding calcium nitrate and ammonia which are easily dissolved in water. Removal of calcium hydroxide produces voids or pores within the concrete. These voids weaken the strength of concrete [8].

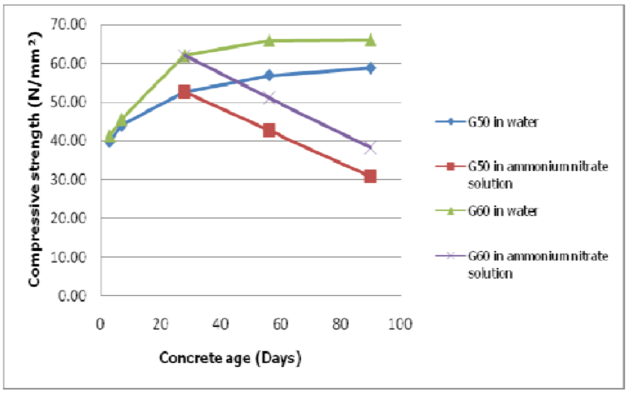

Fig. 1 Compressive strength of concrete immersed in water and ammonium nitrate solution with different ages

B. Water Absorption

Water absorption identifies the capability of concrete to absorb water. The procedures are complied with ASTM C642 [11]. The results for the water absorption are shown in Fig. 2. The water absorption decreased with concrete age for both concrete type G50 and G60 cured in water. After immersion in ammonium nitrate solution, concrete type G50 and G60 absorbed more water than those cured in water. The increased absorption rate with leaching time was similar with results reported by Agostini et al. [12]. The capability of concrete type G50 to absorb water was higher than concrete type G60. The difference between the water absorption of concrete treated in ammonium nitrate solution and water at 56 days was 0.75% for concrete type G50. The difference kept increasing to 1.92% at 90 days. For concrete type G60, the difference was lower than that of concrete G50. It recorded a difference of 0.69% compared to those immersed in water at the age of 56 days. At 90 days, it was 1.27% higher than those immersed in water.

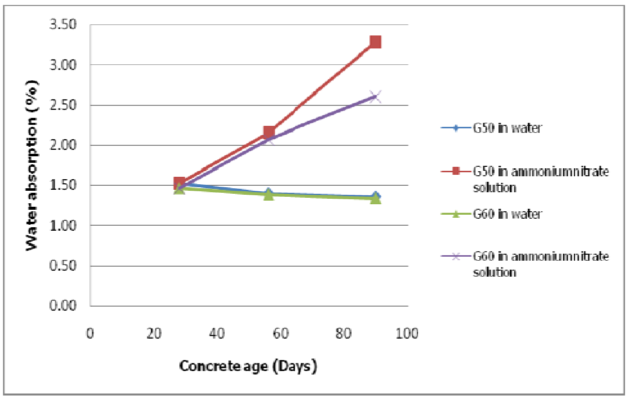

Fig. 2 Water absorption of concrete immersed in water and ammonium nitrate solution with different ages

The average water absorption of concrete type G50 and G60 was higher than those cured in water. It may be due to the dissolution of calcium hydroxide caused by ammonium nitrate solution. Removal of calcium hydroxide introduces more voids within concrete and increases the porosity of concrete. As porosity increases, the diffusion coefficient of calcium is also increased leading to higher rate of hydrates being dissolved. This results in the modification of microstructure of the concrete, causing an increase in permeability and a decrease in bulk density [13].

C. Volume of Permeable Voids (VPV)

The procedures of VPV test are complied with ASTM C642 [11]. The results for volume of permeable voids are shown in Fig. 3. VPV value for concrete type G50 and G60 decreased as the curing age in water increased. The ammonium nitrate solution caused the permeable of concrete to increase, therefore, seriously affecting the durability of the concrete. The difference of VPV value of concrete immersed in water and ammonium nitrate solution at 56 days was about 1.12% for concrete type G50. The difference increased to 2.33% at 90 days immersion. The increase in water absorption was due to removal of calcium hydroxide within concrete pore. For concrete type G60, the VPV value of concrete treated with ammonium nitrate increased with immersion time, however, the increase in VPV was lower than that of concrete type G50. It differs about 0.87% at 56 days compared with those immersed in water. The VPV value recorded at the age of 90 days shows an increment of 2.13%.

The VPV value of both concrete increased with the immersion period. The values were also higher than those immersed in water. It may be due to dissolution of calcium hydroxide in concrete pore. The reduction in concentration of ions in the pore solution forced the dissolution of calcium hydroxide. This resulted in increased of material porosity, permeability and reduced mechanical properties [14]. Calcium hydroxide acts as hydration product which fills in the pore system within the concrete. Removal of calcium hydroxide from the pore increases the voids causing the concrete to become more permeable.

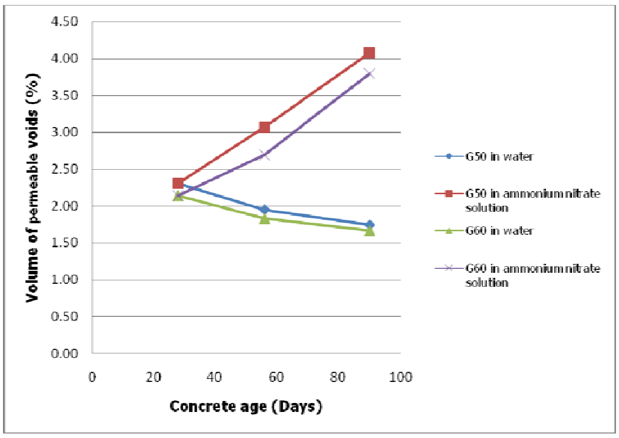

Fig. 3 VPV values of concrete immersed in water and ammonium nitrate solution with different ages

D. Sorptivity

Sorptivity test measures capillary suction of concrete when it is in contact with water. It is an index of moisture transport into unsaturated specimens; therefore it had been recognised as an important index of concrete durability [15]. The procedures used are as described by Chan and Ji [16]. Fig. 4 shows the results of sorptivity of concrete type G50 and G60. The sorptivity coefficients of concrete treated with ammonium nitrate solution increased with the time of immersion. There was a difference of about 27.4% in sorptivity at the age of 56 days for concrete type G50 treated in ammonium nitrate compared with those immersed in water at the same age. At the age of 90 days, the difference in sorptivity coefficient increased to as much as 34.8%. For concrete type G60, the difference was only 9.3% for ammonium nitrate treated concrete at the age of 56 days compared to those immersed in water at the same age. Subsequently, the sorptivity increased 22.0% at 90 days of age.

The increasing of sorptivity coefficient is caused by the modification of pore structure. Ammonium nitrate removes calcium hydroxide from the concrete pore. This produces more voids within the concrete, thus increasing the ability to absorb more water. According to Haga et al. [17], the pore volume became larger with leaching periods. The increased of pore volume became larger with a larger decreased in the quantity of calcium hydroxide. The increased in pore volume were attributable to the dissolution of calcium hydroxide. The rate of water absorption by concrete type G60 is slower than that of concrete type G50. It may be due to the lower dissolution of calcium hydroxide in concrete type G60 compared to that of concrete type G50.

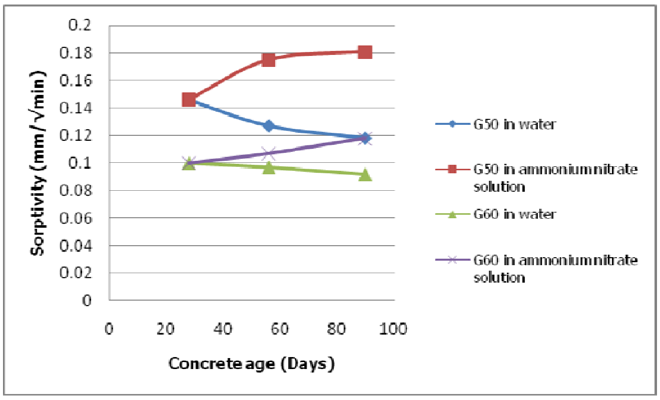

Fig. 4 Sorptivity of concrete immersed in water and ammonium nitrate solution with different ages

E. pH Measurement

The procedure is referred to Geotechnical Engineering Bureau [18]. The results of pH values for concrete type G50 and G60 immersed in water at specified age are shown in TABLE III. For concrete type G50, the pH value decreased after immersed in ammonium nitrate solution for 56 days. Initially, the pH value is 10.81 for the depth between 0-5 mm at the age of 56 days. The difference in pH value between concrete immersed in ammonium nitrate and water was recorded to be 11.40%. Then, the difference of pH value dropped when testing depth increased. The pH value decreased from 4.75% to 0.50% for the depth of 5-10 mm until 20-25 mm. For concrete age of 90 days, the result shows a decrease of pH value from 13.70% to 0.98%.

The pH value for concrete type G60 also decreased with immersion period. It recorded pH 11.30 at the age of 56 days and pH 11.13 at the age of 90 days for the depth of 0-5 mm. The reduction was about 7.53% and 9.00% at 56 days and 90 days concrete age, compared with those immersed in water. The reduction of pH value became smaller when testing was conducted for further depth. It shows a decreasing of 0.33% and 0.57% in pH value for the testing depth of 20-25 mm at the age of 56 days and 90 days.

Decreasing in pH values when immersed in ammonium nitrate solution may due to the dissolution of hydrates in concrete. Kamali et al. [19] indicate that the lower the pH of the aggressive water and higher the concentration gradient, the diffusion of hydroxyl ions would be significant. The ammonium nitrate solution led to a pure dissolving corrosion by a neutralization reaction. This showed that the pH value in the attacked part of the specimens was reduced by the neutralization reaction [2].

TABLE III
RESULTS OF PH VALUE OF CONCRETE AT DIFFERENT AGES

Concrete Type	Depth (mm)	Age (Days)			
		56		90	
		Water	NH_4NO_3	Water	NH_4NO_3
G50	0-5	12.20	10.81	12.20	10.53
	5-10	12.23	11.65	12.23	11.34
	10-15	12.24	11.91	12.25	11.74
	15-20	12.26	12.02	12.26	11.89
	20-25	12.27	12.21	12.27	12.15
G60	0-5	12.22	11.30	12.23	11.13
	5-10	12.25	12.09	12.25	12.03
	10-15	12.27	12.17	12.27	12.13
	15-20	12.27	12.24	12.28	12.22
	20-25	12.29	12.25	12.30	12.23

F. Degradation Depth Measurement

The degradation depth is defined as the distance from inner front to the external surface of the material. It increases with the dissolution of hydrates [19]. The procedures are referred to Nguyen et al. [20]. Fig. 5 shows the results of degradation depth for both concrete type G50 and G60. It can be observed that the degradation depth increased with immersion time. The slope of the graph for concrete type G60 was less steep than that of concrete type G50. It shows a smaller value of coefficient k with 0.67 compared with coefficient k for concrete G50 which was 0.77.

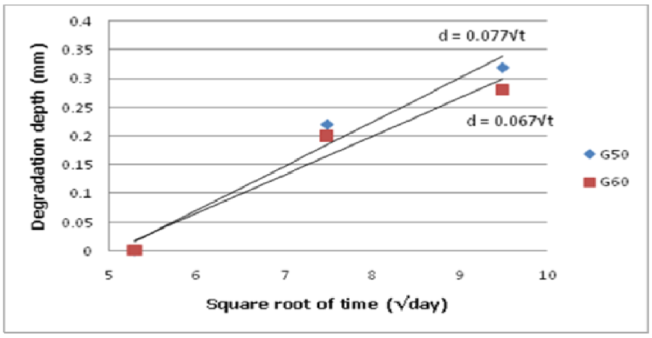

Fig. 5 Graph of degradation depth versus square root of time

According to Nguyen et al. [20], the leaching depth increased with leaching duration. Schneider and Chen [2] found out that the degradation depth depended on the initial strength of the specimens. Concrete with higher strength had lower value of coefficient k. Based on this research, the compressive strength at the age of 28 days for concrete type G50 is 52.67 N/mm^2 while concrete type G60 recorded 62.01 N/mm^2. The degradation depth of concrete type G60 is 0.067 X square root of time while concrete type G50 recorded 0.077 X square root of time. It shows that concrete type G60 had lower value of coefficient k than concrete type G50. This indicates that concrete type G50 was more susceptible to degradation caused by ammonium nitrate solution compared to concrete type G60.

IV. Conclusion

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

1) Concrete type G60 performs better and is less susceptible to damage compared to concrete type G50 when leached by ammonium nitrate solution.
2) The loss of strength of concrete type G60 is less than that of concrete type G50 after immersed in ammonium nitrate solution for a certain period.
3) After the leaching process, the durability properties of concrete type G60 was higher than that of concrete type G50.
4) The pH measurement shows that the reduction in pH values for concrete type G60 is lower than that of concrete type G50 when they were subjected to immersion in ammonium nitrate solution for different immersion time.
5) The rate of degraded depth for concrete type G60 is less than that of concrete type G50.

References

[1] British Standards Institution. 1997. Structural Use of Concrete, *Code of Practice for Design and Construction*. BS8110. BSI, London. Pp. 122.
[2] Schneider, U. & Chen, S.-W. 1999. Behavior of high-performance concrete (HPC) under ammonium nitrate solution and sustained load. America Concrete Institute, *ACI Materials Journal* 96(1): 47-51.
[3] Ukraincik, V., Bjegovic, D. & Djurekovic, A. 1978. Concrete corrosion in a nitrogen fertilizer plant. In Peter J. Sereda & G. G. Litvan. Durability of Building Materials and Components: *Proceedings of the First International Conference*. Ottawa, Canada. Pp. 397-409.
[4] Lea, F.M. 1965. The action of ammonium salts on concrete. *Magazine of Concrete Research* 17(52): 115-116.
[5] Maltais, Y., Samson, E. & Marchand, J. 2004. Predicting the durability of Portland Cement systems in aggressive environments: laboratory validation. *Cement and Concrete Research* 34(9): 1579–1589.
[6] Barr, B.I.G. 2003. *Failure of concrete structures*. Cardiff, UK: University of Wales.
[7] ASTM C150/C150M – 11 “Standard Specification for Portland Cement.”
[8] Shan Somayaji. 2001. *Civil Engineering Materials*-Second Edition. New Jersey: Prentice Hall.
[9] *BS 1881: Part 116:1983*. 1983. Method for Determination of Compressive Strength of Concrete Cubes. London: British Standards Institution.
[10] Carde, C. & Francois, R. 1997 (a). Aging damage model of concrete behavior during the leaching process. *Materials and structures constructions* 30: 465-472.
[11] ASTM C642. 2002. Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. *Annual Book of ASTM Standards* 2002, 04.02. Philadelphia: American Society for Testing and Materials.
[12] Agostini, F., Lafhaj, Z., Skoczylas, F. & Loodsveldt, H. 2007. Experimental study of accelerated leaching on hollow cylinders of mortar. *Cement and Concrete Research* 37: 71-78.
[13] Yang, H., Jiang L., Zhang Y., Pu, Q., Xu, Y. 2012. Predicting the calcium leaching behavior of cement pastes in aggressive environments. *Construction and Building Materials* 29: 88-96.
[14] Jain, J., & Neithalath, N. 2009. Analysis of calcium leaching behavior of plain and modified cement pastes in pure water. *Cement & Concrete Composites* 31: 176-185.
[15] Dias, W.P.S. 1995. Sorptivity Testing for Assessing Concrete Quality. *Proc. Int. Conf. on Concrete under Severe Exposure Conditions* (CONSEC '95). Spon, London. Pp. 433-442.
[16] Chan, SYN. and Ji X. 1998. Water sorptivity and chloride diffusivity of oil shale ash concrete. *Construct Build Mater* 12(4): 177-183.
[17] Haga, K., Sutou, S., Hironaga, M., Tanaka, S. & Nagasaki, S. 2005. Effect of porosity on leaching of Ca from hardened ordinary portland cement paste. *Cement and Concrete Research* 35: 1764-1775.
[18] *Geotechnical Engineering Bureau*. 2007. Test Method for the determination of pH value of water or soil by pH meter. New York State Department of Transportation.
[19] Kamali, S., Gerard, B. & Moranville, M. 2003. Modelling the leaching kinetics of cement-based materials: Influence of materials and environment. *Cement and Concrete Composites* 25: 451-458.
[20] Nguyen, V. H., Colina, H., Torrenti, J.M., Boulay, C. & Nedjar, B. 2007. Chemo mechanical coupling behavior of leached concrete part I: Experimental results. *Nuclear Engineering and Design* 237: 2083-2089.