Emmanuel Wayne Sookree, et. al. International Journal of Engineering Research and Applications
www.ijera.com
ISSN: 2248-9622, Vol. 10, Issue 7, (Series-V) July 2020, pp. 16-23

RESEARCH ARTICLE OPEN ACCESS

Effect of High-Volume Limestone Powder and Fly Ash on the Calcium Leaching Resistance of Roller Compacted Concrete

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ABSTRACT
Roller compacted concrete (RCC) is a type of concrete which is dry in nature and has no slump. Traditionally, high volumes of fly ash were used as cement replacement material in RCC. However, fly ash is gradually becoming scarce and can be quasi-inexistent in some regions. The usage of limestone powder is highly encouraged for its positive effects on the environment, availability, and affordable prices. Hydraulic concrete structures such as dams are at high risk of leaching calcium ions. The influence of high-volume limestone powder on the calcium leaching resistance and mechanical performance of RCC was investigated. Both limestone powder and fly ash in high volumes were used in the mix designs. A water-to-binder ratio of 0.5 was kept constant and 0.6% of water reducing admixture based on the cement weight was used. Calcium leaching tests were conducted over a period of 60 days. The dissolution process of calcium hydroxide was accelerated using ammonium chloride with a concentration of 1mol/L. The experiments revealed that a 40% addition of limestone powder caused a dilution effect resulting in increased porosity and drastically lowering the concrete's splitting tensile strength by at least 45.8% relative to the other mix designs. However, the concentration of calcium ions was the lowest for that group possibly due to a higher degree of compactness and better pore structure affecting the dissolution and diffusion rate. For optimum mechanical performance and resistance against calcium leaching, the content of limestone powder should be within 20 to 30%.
Keywords: Roller compacted concrete, high-volume limestone powder, fly ash, calcium leaching resistance, dilution effect.

Date of Submission: 06-07-2020 Date of Acceptance: 21-07-2020

I. INTRODUCTION

Roller compacted concrete or RCC for short, is a very dry and stiff type of concrete. It is popular for its economic aspect and time-efficiency. RCC is very convenient for large-scale construction projects such as pavements (RCCP) and dams (RCCD). It is placed in several layers, requiring the use of heavy duty compactors to attain a required density and surface texture. The difference between RCC and conventional concrete (CC) is the proportioning of materials. Generally, RCC is characterized by low cement levels and high contents of aggregates. Traditionally, high volumes of fly ash were used in RCC to improve the concrete mechanical and physical properties as well as reducing the high cement demands [1-5]. However, in this new era, fly ash is gradually being replaced with other mineral admixtures such as limestone powder, silica fume, and pumice powder [6 - 13]. Countries such as China and the US are still heavily dependent on the burning of coal to generate electricity. This trend, however, will definitely change direction in the near future as developed and developing countries invest considerably in renewable and environment-friendly sources of energy such as hydropower, solar and wind energy which will inevitably hinder the production and availability of fly ash worldwide. Not to mention that fly ash is already scarce in some places such as the North-Western regions of China. Therefore, studying the effects of different mineral admixtures on the mechanical performance and durability of concrete is vital for future development projects.The use of limestone powder is highly encouraged nowaydays not only for its ability to reduce the carbon footprint in the concrete industry, but also for its abundance and cost-effectiveness. The contributions of limestone powder to the performance of concrete are dependent on its particle size [14], surface morphology [15], and amount [16].

Concrete structures such as dams are continually exposed to water, weather conditions, and pollutants causing leaching of calcium hydroxide (Portlandite). Previous studies have shown that both calcium hydroxide and calcium silicon hydrate are prone to leaching in water [17 – 20]. The leaching process may be very slow, but the impact can be substantial over a long period of time. Dissolution and diffusion are the two processes that affect the equilibrium state of hydration products in concrete. Dissolution refers to the disintegration of solid phases while diffusion is the movement of a substance from a high to low concentration. Calcium leaching leads to a reduction in alkalinity, mass, and strength [21]. A loss in mass correlates to increased porosity and permeability of the concrete [22]. Dissolution of calcium hydroxide in particular, increases the macro porosity of concrete in the short term [23]. The durability of concrete is mainly attributed to its ability to prevent infiltration of water. The effect of high-volume limestone powder on the calcium leaching resistance of RCC is scarce in literature. Therefore, it is necessary to conduct studies related to that matter which will help to better understand the behaviors of hydraulic concrete structures built with RCC using limestone powder in large quantities.

1.1 Research Objective

The main objective of this study is to evaluate the effect of high-volume limestone powder on the calcium leaching resistance and how it affects the mechanical performance of RCC.

1.2 Methodology

Casting, curing, and test methods were all carried out according to the specifications provided in DL/T 5433-2009 [24]. A total of 24 cubic specimens (150 mm x 150 mm x 150 mm) were prepared. 12 specimens of 28-day curing age were each used for the calcium leaching and splitting tensile strength tests respectively. The experimental values were averaged from three measurements. The calcium leaching test was performed over a period of 60 days, whereby samples of the solutions were taken and measured every 10 days to find out the concentrations of calcium ions. Since leaching in de-ionized water is a very slow process, a chemical method is employed to speed up the chemical dissolution of calcium hydroxide and diffusion of calcium ions. To that end, a concentration of 1 mol/L of ammonium chloride (NH_4CL) was mixed with the water into which the specimens were immersed (Fig. 1(a)). To study the effect of the mineral admixtures on the mechanical performance of RCC, the splitting tensile strength of cubic specimens before and after the leaching test was investigated through the use of a universal testing machine coupled with two steel loading plates (Fig. 1(b)).

(a)

(b)

Fig. 1. Test methods: (a)Calcium leaching test, (b) Splitting tensile strength test

II. EXPERIMENTAL PROGRAM

2.1 Materials

Portland cement 42.5Type MH (Moderate heat of hydration),Grade II fly ash, limestone powder, river sand and crushed stones were used to prepare the RCC specimens. The crushed stone have two gradations, namely No. 1 and No. 2 with diameters ranging from 5 to 20 mm and 20 to 40 mm respectively. The weight of crushed stones is equally distributed among the two gradations. The sand and water contents were not changed. A water-to-binder ratio of 0.5 was kept constant for all mix designs and the amount of water reducing admixture corresponds to 0.6% of the cement weight as per the recommendation of the supplier. Tables 1 to 5 below contain Chinese Standards where applicable, pertinent to the quality control of the materials used in this study.

Table 1. Physical and chemical properties of P. MH42.5

Properties		P. MH42.5	GB200-2017	Chemical Composition	P. MH42.5	GB200 - 2017
Density (kg/m^3)		3260	/	SiO_2	21.5	/
Specific surface area (m^2/kg)		308.4	≥ 250	Al_2O_3	4.44	/
Normal consistency (%)		22.4	/	Fe_2O_3	5.04	/
Initial setting time (h)		2h06min	$\geq$1h	CaO	61.15	/
Final setting time (h)		4h03min	$\leq$ 12h	MgO	4.94	$\leq 5.0^a$
Stability		Qualified	Qualified	SO_3	1.90	≤ 3.5
Hydration heat	3d	248	$\leq$251	R_2O	0.29	$\leq 0.60^b$
(kJ/kg)	7d	291	$\leq$293	Loss on ignition	1.11	≤ 3.0

Note: "a" means that the Magnesium Oxide content is allowed to reach 6% if the cement pressure test is acceptable; "b" states that if a potentially hazardous alkali reactive aggregate is to be used, the alkali content in cement cannot exceed a maximum of 0.6%.

Table 2. Physical and chemical properties of Grade II fly ash

Properties	Grade II fly ash	DL/T 5055-2007	Chemical Composition	Content (%)
28d compressive strength (%)	80	$\geq$70	SiO_2	46.11
			Fe_2O_3	7.52
Density (kg/m^3)	2100	/	Al_2O_3	30.77
Fineness (%)	20	$\leq$ 25.0	CaO	6.64
			MgO	3.92
Specific surface area (m^2/kg)	305	/	K_2O	0.54
			Na_2O	0.42
Water Requirement Ratio	0.95	$\leq$ 1.05	Alkali content	0.77
Moisture content	0.12	$\leq$1.0	Loss on Ignition	2.51

Table 3. Physical and chemical properties of limestone powder

Properties	Index
Density (kg/m^3)	2470
Specific surface area (m^2/kg)	292
Activity index (%)	69
$CaCO_3$ (%)	82.5
SiO_2 (%)	12.2
Al_2O_3 (%)	1.58
Fe_2O_3 (%)	2.34
MgO (%)	0.46
K_2O (%)	0.35
Other (%)	0.57

Table 4. Physical properties of fine and coarse aggregates

Properties	Coarse aggregate		DL/T 5144- 2015 (Coarse aggregate)	Fine aggregate	DL/T 5144- 2015 (Fine aggregate)
	No.1	No. 2			
Fineness modulus	/	/	/	3.08	2.2 ~ 3.0
Saturated surface dry density (kg/m^3)	2680	2670	$\geq$2550	2640	$\geq$2500
Saturated surface dry water absorption	0.85	0.49	$\leq$2.5	0.54	/
Toughness (%)	1.7	1.3	$\leq$5	1.52	$\leq$8
Crushing index (%)	20.1	5.4	$\leq$20	/	/
Sulphate content (%)	0.1	0.1	$\leq$0.5	0.03	$\leq$1

Table 5. Physical properties of water-reducing admixture

Properties		JM-II set-retarding high efficiency water-reducing admixture	DL/T 5100 - 2014
Water reducing rate (%)		21.6	≥ 15
Bleeding rate (%)		83.0	≤100
Gas content (%)		1.0	≤3.0
Setting time difference (min)	Initial	+130	+120 ~ +240
	Final	+150	+120 ~ +240
Compressive strength ratio	7d	1.67	≥1.25
	28d	1.54	≥1.20
Alkali content (%)		7.34	/

2.2 Mix Proportioning

The mixing process was done in the following order: (1) Cement/Mineral admixtures, coarse and fine aggregates were mixed for 1 min in a laboratory concrete mixer.(2) Potable water and the water reducing admixture were mixed for at least 1 min before adding the mixture to the rest of the materials inside the concrete mixer.(3) Afterwards, all the materials were mixed for a total of 2 min to guarantee a homogeneous mixture. The aforementioned steps were carried out for all mix designs. The material proportions and identification of the specimens are given in Table 6 below. The changes in volume of cementitious materials with different proportions of the mineral admixtures were negligible and therefore not considered in this study for further analysis and discussion. The mix designs were assumed to have the same consistency.

Table 6. Mix Designs

Identification	Material composition (kg/m³)								
	w/b	Cement	Limestone powder	Fly ash	Water	Sand	Coarse aggregate No. 1	Coarse aggregate No. 2	Water reducing admixture
C60L10F30	0.5	100.8	16.8	50.4	84	769.4	717.25	717.25	0.6048
C60L20F20	0.5	100.8	33.6	33.6	84	769.4	717.25	717.25	0.6048
C60L30F10	0.5	100.8	50.4	16.8	84	769.4	717.25	717.25	0.6048
C50L40F10	0.5	84	67.2	16.8	84	769.4	717.25	717.25	0.504

Note: C – Portland cement; L – Limestone powder; F – Fly ash.

2.3 Casting and Curing Procedures

Once the mixing process was completed, the cubic molds were filled with the fresh concrete. A steel plate weighing 5 kg with a surface area slightly smaller than the inner dimensions of the molds was attached to a vibrating hammer and used to compact the RCC specimens which consisted of 3 layers. Each layer was compacted for about 30 seconds. After casting, test specimens were placed in a moist curing room for 48h at a temperature of 20 ± 5°C and relative humidity of 90%. The specimens were then gently removed from the molds and left in the curing room for a total of 28 days.

III. TEST METHOD

3.1 Calcium Leaching and EDTA Titration

Calcium leaching test was performed using ammonium chloride which can accelerate the dissolution process hundreds of times faster than using de-ionized water. Samples of the solutions were taken every 10 days for a total of 60 days and the concentrations of calcium ions were measured using Ethylenediaminetetraaceticacid titration. Ethylenediaminetetraaceticacid (EDTA) is a molecule that binds itself to minerals and metals. EDTA titration, also known as complexometric titration is a method that forms a complex with calcium and magnesium ions. A blue dye called Patton and Reeder's indicator (PR) was used as an indicator. The PR indicator changes color from blue to pink/red when mixed with the solution containing calcium ions and reverts to blue after the endpoint has been reached. The steps and measurements undertaken for the titrations were as follows: (1) Pipette 10 mL of the solution containing the calcium ions into a conical flask. (2) Add 40 mL of distilled water to the solution. (3) Measure and mix 0.1g of PR indicator and swirl to dissolve the indicator. (4) Open the valve of the burette containing the EDTA titrant allowing it to slowly drip into the solution. (5) Swirl the conical flask while mixing the titrant until the indicator changes from pink/red to blue characterizing the endpoint.The following relationship was used to obtain the concentration of calcium ions in the solutions:

$$(M_1V_1)_{acid} = (M_2V_2)_{base} \quad (1)$$

Where, M_1 = Molar concentration of the acid solution (in mol/L), V_1 = Volume of acid solution (in mL), M_2 = Molar concentration of base solution (in mol/L), and V_2 = Volume of base solution (in mL).

3.2 Splitting Tensile Strength

The tensile strength of concrete under uniaxial stress is rarely determined through a direct tensile test due to the difficulties involved in its execution and lack of precision in the results. Instead, splitting tensile and flexural tests are used as indirect methods to obtain the tensile strength of concrete. The center lines of the specimens and loading steel plates were located and marked (Fig. 1(b)). After proper alignment, both loading steel plates and specimens were tightened in a universal testing machine. The loading rate applied was in the range of 0.05 to 0.35 Mpa/s so that failure would occur within 1 to 10 min. The splitting tensile strength of a cubic concrete specimen can be calculated as follows:

$$f_{cts} = \frac{2P}{\pi l d} \quad (2)$$

Where, f_{cts} = Splitting tensile strength (in MPa), P= Load at failure (in N), l = Thickness (in mm), and d = Height of specimen (in mm).

IV. RESULTS AND DISCUSSION

4.1 Calcium Leaching

The calcium leaching test results are presented in Fig. 2 below. The cumulative concentrations of calcium ions after 60-day leaching test are 3.33, 3.51, 3.52, 3.16 mol/L for C60L10F30, C60L20F20, C60L30F10, and C50L40F10 respectively. Among the four groups, C50L40F10 has the lowest concentration of calcium ions indicating that the damage sustained by its pore structure was not as severe as that of the other mix designs throughout the whole duration of the leaching test. Pore refinement is actually improved when the particle size of a mineral admixture is equal to or smaller than cement particles also known as the filler effect. The specific surface area or Blaine's fineness of fly ash and limestone powder are quite comparable to cement with a relative difference of 1.1% and 5.3% respectively. These values are rather small. Therefore, the mineral admixtures having a negative impact on the pore structures is highly unlikely. It would appear that with increasing limestone powder content (from 20% to 30%) the diffusion rate of calcium ions increases. Strangely enough, beyond 30%, the concentration of calcium ions decreases. This anomally could be due to a different degree of compactness resulting in a poor pore structure which could have affected the diffusion rate.

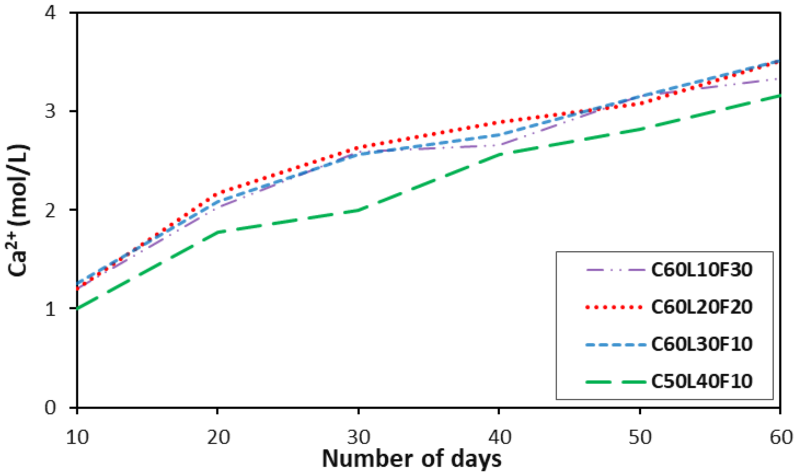

Fig. 2. Concentration of leached calcium ions

4.2 Splitting Tensile Strength

The splitting tensile strength test results are shown in Fig. 3 below. The values recorded before and after the 60-day leaching test are 2.74, 2.62, 2.53, 1.37 and 0.95, 1.12, 0.62, 0.56 MPa for C60L10F30, C60L20F20, C60L30F10, and C50L40F10 respectively. When fly ash is used, a secondary hydration is observed due to its late age properties resulting in the production of additional calcium silicon hydrate, also known as C-S-H gel. The C-S-H gel is the main hydration product and is responsible for the overall strength development in concrete. A 30% fly ash content (C60L10F30) has a splitting tensile strength slightly higher than the mix designs with a maximum limestone powder content of 30%. It is clear that a limestone powder content of more than 30% leads to a severe drop in strength (Fig. 3) which could be attributed to a reduction of C-S-H gel. Limestone powder does not have cementitious or pozzolanic properties. A high dosage can lead to increased hydration degree due to the excess of free water reacting with cement particles also known as the dilution effect. As a result, the water-to-cement ratio is elevated which in turn, increases the porosity of concrete. When compared to C60L30F10, C50L40F10 has almost half of the splitting tensile strength. The difference in splitting tensile strength relative to the original values (before leaching test) are equal to 65.3%, 57.3%, 75.5%, and 59.1%. Although, the strength development for C50L40F10 is quite low, its relative change in strength after 60 days is not as bad as C60L30F10 which registered the worst performance. Leaching of calcium ions increases the porosity of cement-based material, thus resulting in degradation of the pore structure. With the increased porosity, the concrete matrix is weakened which directly affects its strength.

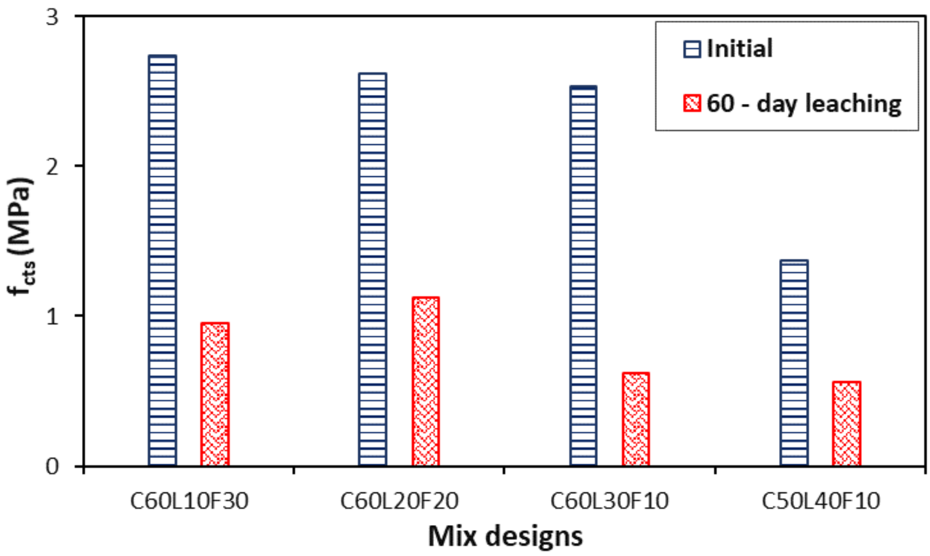

Fig. 3. Splitting tensile strength of RCC specimens measured before and after calcium leaching test

V. CONCLUSIONS

In this study, the effect of limestone powder and fly ash on the calcium leaching resistance and splitting tensile strength of RCC was investigated. From the data obtained experimentally, the following conclusions were drawn:

(1) A limestone powder content of more than 30% caused a dilution effect resulting in major loss of splitting tensile strength. For optimum residual strength after calcium leaching test, a limestone powder content around 20% is recommended as evidenced by the results obtained.

(2) The differences in Blaine's fineness between cement, limestone powder, and fly are quite negligible. The particle size of a mineral admixtureplays an important role in pore refinement of the concrete matrix. However, the concentrations of calcium ions for the mix designs containing up to 30% limestone powder showed contradictory results, possibly due to a lower degree of compactness and poor pore structure, hence facilitating the infiltration of water, dissolution and diffusion of calcium ions warranting further investigations.

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