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Performance of Concrete Containing Locust Bean Pod Ash and Metakaolin as Cement Replacement

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Abstract - Locust bean pod (LBP) is a pozzolanic African agricultural waste originated from locust bean tree (Parkia biglobosa). This study presents strength and extreme pH Resistance of locust bean pod ash (LBPA) concrete containing metakaolin (MK) as cement replacement material (control, OPC-LBPA, and OPC-LBPA-MK). The LBP and kaolin were thermally digested into LPB ash (LBPA) and MK. Ordinary Portland cement in concrete was replaced with LBPA by mass. The workability and setting times were determined. The strength and extreme pH resistance (HCl and H_2SO_4 acids, and sulphate) were assessed. Properties of the concrete were statistically analyzed and optimized using response surface methodology (RSM). As the LBPA content increased, the workability was reduced. Further, the 5% LPBA replacement showed the greatest improvement for the binary system while combined 20% (5% LBPA and 15% MK) replacement level gave the best performance for the ternary system at 90 days. Additionally, both blends improved the performance of concrete against acids and sulphate. The study concludes that up to 35% of OPC could be replaced using 20% of LBPA and 15% MK in a ternary system for structural concrete. LBPA along with MK should be utilized in the production of structural concrete for low-cost construction.

Key words: Compressive Strength; Extreme Ph; Agricultural Waste; Locust Bean Pod Ash; Metakaolin; Cementitious Material.

Highlights:

- ***LBP is a pozzolanic African agricultural waste originated from locust bean tree.***
- ***The concrete strength containing LBPA and MK was assessed.***
- ***The effect of extreme pH on LBPA and MK concrete strength was investigated.***
- ***The variables were statistically analyzed and optimized via RSM.***
- ***LBPA combined with MK can be used as low-cost cement replacement material.***

I. INTRODUCTION

Continuous generation of agricultural wastes creates environmental and economic problems, hence the need for upcycling of such wastes. The construction industry in recent times has been able to utilize these agricultural wastes in cement-based products like concrete which is most frequently employed construction material globally (Mindess et al., 2003; He et al., 2020). Concrete is made of Portland cement (OPC), aggregates, water and in some cases admixtures (Neville, 2011). However, continues production is not sustainable with depletion of natural resources used to produce concrete. Cement production increased to 3,500 million tons in 2020, and by 2050, it is anticipated to reach 3,700 to 4,400 million tons (Madeleine, 2012). Also, around 110 kWh of energy and 1,500 kg of basic materials are required to make a ton of cement (Ahmad et al., 2021). Additionally, OPC which is concrete's most crucial component is expensive, and its production requires high energy and is deleterious to the environment due to greenhouse gases emission. According to estimates, the production of cement alone produces 1.350 billion tons of greenhouse emissions annually (Cleetus et al., 2018). The construction industry alone contributes to 50% global carbon dioxide (CO_2) emission (Arrigoni et al., 2020). To reduce cement usage in concrete, supplementary cementitious materials (SCMs) have been used to replace OPC in concrete with corresponding positive results (Ayub et al., 2014). SCMs could be from natural sources, industrial by-products or agricultural wastes. Agricultural wastes are readily available at little or no cost and due to the qualities of concrete containing such with tremendous potential, the use of agricultural wastes as SCMs has increased in recent times (Ikumapayi, 2016).

The African locust bean (*Parkia biglobosa*); a perennial tree species native to the west African savannah is utilized for a variety of purposes including food, condiments, medicine and manure (Adama et al., 2013). The harvested fruits have two components: the seed and yellow pulp which make up 61% of the fruit with the pods (waste material) accounting for 39% by weight (Bello et al., 2019). The pods are agricultural wastes which constitute environmental and economic societal problems. Nearly 201,000 tons of locust bean fruits are harvested annually in northern part of Nigeria alone (Adedokun & Oluremi, 2019). The pods have been upcycled in different forms (powder, extract and ash) in the construction industry for soil stabilization, production of sandcrete blocks, mortar and concrete thereby leading to reduction in construction cost and conservation of energy and environment. (Aguwa et al., 2016; Aliyu et al. 2018; Auta & Kabiru, 2020).

Research works have found LBPA useable with great promise in stabilization of soil and improving the properties of mortar and concrete (Adama & Jimoh, 2012; Adama et al., 2013; Akpenpuun et al., 2019; Yalley, 2019; Auta & Kabiru, 2020). A summary of selected studies conducted using LBPA as cement replacement is given in table 1. However, majority of the investigations are limited to determination of the optimal percentage replacement required to achieve a target compressive strength of concrete up to a maximum substitution level of 50% in binary and biogenic ternary blends without consideration to durability and other properties. Incorporation of LBPA affects the quality of concrete. All studies reported a limitation in LBPA use in concrete production; LBPA concrete produces compressive strength less than the control concrete at 28 days (Afolayan et al., 2018; Ali et al., 2019). The studies also revealed that inclusion of LBPA beyond 10% replacement level drastically reduces compressive strength and other properties of concrete owing to low pozzolanic activity. Additionally, the long-term strength of LBPA concrete has not been established as most studies did not go beyond 28 days curing period. There is therefore the need to mitigate this limitation by evaluating the long-term strength of LBPA concrete and complementing LBPA with a highly reactive pozzolan in a ternary system in order to improve its performance in concrete.

MK is a pozzolanic substance created by calcining Kaolin at temperature range of 500 to 900°C (Zhang & Malhotra, 1995; Rashad, 2013; Wang et al., 2019). The MK used is this study was acquired from the heating of locally sourced Kaolin from Alkaleri, Bauchi state, Nigeria. MK was chosen for this study due to the availability of Kaolin in Nigeria at little or no cost, thus leading to cost reduction. Nigeria has about two billion metric tons of underutilized kaolin spread across all over the country (Raw Materials Research and Development Council, 2010). Additionally, MK is an efficient pozzolan in cement-based products because it increases strength, reduces drying shrinkage, and increases longevity (Khatib et al., 2018; Eldin et al., 2020). Up to 15% of OPC could be substituted by MK in concrete (Bright Singh & Murugan, 2022). Sullivan et al. (2020) reported very strong chemical resilience, low chloride-ion penetrability, increased coefficient of thermal expansion values and lowered drying shrinkage by ternary mixtures containing MK. The authors investigated a ternary system at cement replacement level of 45% using 15% metakaolin and 30% slag replacements at 0.43 water binder ratio.

It is pertinent to state that LBPA is a less reactive pozzolan while MK is highly reactive (Glavind, 2009). When a less reactive pozzolan is combined with a more reactive pozzolan in a ternary mix, there is synergy between the pozzolans resulting in increased strength (Isaia, 1999). It is reported in literature that ternary mixed cements outperform standard binary blended cements or OPC. In order to mitigate the aforementioned limitation of LBPA in concrete, LBPA was used alongside locally produced MK to produce a ternary concrete. This is because MK has been used in ternary systems in conjunction with other pozzolans in production of concrete with improved properties (Ninan & Nazeer, 2016; Dadsetan & Bai 2017; Sullivan et al., 2020). The performance of OPC, LBPA and MK in a ternary system is not known as adequate studies have not been carried out using ternary system containing OPC, LBPA and MK in concrete production. It is against this backdrop that this study was conducted to determine how these ternary cementitious systems influence concrete characteristics. The main purpose of this paper was to study and compare fresh, mechanical and durability properties of OPC-LBPA concrete and improve its performance by complementing it with MK in ternary cementitious systems. Other objectives are reduction of construction cost, cement consumption while ensuring efficient agricultural waste management. Binary and ternary combinations of OPC, LBPA and MK with various combinations were investigated.

The influence of LBPA and MK on fresh and hardened properties of the concrete including slump, compacting factor, strength (compressive, splitting tensile and flexural) as well as resistance to acids and sulphate were examined. Moreover, some properties of the concrete were modelled and optimized.

Table 1: Summary of selected previous studies using LPBA as reported in the literature.

No.	Authors	W/b Ratio	Method	% Replacement	Properties		Summary of Findings
					Strength (N/mm^2)	pH Resistance	
1	(Ja'e, 2019)	0.53	Cement replacement	0, 5,10,15 and 20%	X	X	Increased consistency, increased water requirement.
2	(Afolayan et al., 2018)	0.55	Cement replacement	0, 5 to 50% in increment of 5%	Compressive: 25, 22.33, 19, 13.5, 10.3, 9.7, 8.5, 6.8, 5.3, 5.1, 4.7	X	Increased compacting factor/slump, decrease in strength with addition of LBPA
3	(Auta et al., 2020)	0.50	Cement replacement	0, 5, 10, 15 and 20%	Flexural: 9.2, 9.0, 7.79, 6.57 and 4.5	X	Increased workability, increased flexural strength with curing time.
4	(Akpenpuun et al., 2019)	0.55	Cement replacement (Mortar)	0, 10, 15, 20 and 30%	Compressive: 22.5, 14.27, 13.0, 14.8, and 10.8	X	Decreased workability, increased initial and final setting times, increased compressive strength up to 15% LBPA replacement.
5	(Ali et al., 2019)	X	Cement replacement	0, 5, 10 and 15%	Compressive: 28.33, 23.0, 22.33, and 13.43	X	Reduction in compressive strength but increased with curing age.
6	(Ndububa & Uloko, 2015)	X	Cement replacement	0, 5, 10, 15, 20 and 25%	Compressive: 22.19, 20.92, 13.70, 12.44, 12.13 and 12.03	X	Decreased compressive strength; strength increased with curing age and decreased water absorption.
7	(Ochola et al., 2021)	X	Cement replacement	0, 5, 10 and 15%	Compressive: 27.54, 24.83, 23.90 and 15.54	X	Reduced compressive strength.
8	(Yalley, 2019)	0.5± 0.02	Cement replacement	0, 40, 50 and 60%	Compressive: 40, 42, 39.8 and 38.2 Tensile: 3.8, 4.5, 4.2 and 3.1	X	Increased compressive, tensile and flexural strengths.
9	(Olubajo, 2020)	0.4	Cement replacement	0, 2.5, 5, 7.5, and 10%	Compressive: 48.18, 46.0, 40.09, 41.92 and 43.18 Flexural:	X	Increased strength with curing age.

					6.80, 6.43, 6.21, 6.03 and 6.99		
10	(Ikumapayi et al., 2019)	0.45	Cement replacement	0, 4, 8 and 12%	X	X	Better drying shrinkage than control at 56 and 90 days.
11	Current Research	0.5	Cement replacement	0, 5,10,15,20,25 and 30%	Compressive, flexural, tensile	√	Presented in this paper.

II. METHODOLOGY

2.1 Materials

The sampling locations for LBP in Makurdi, MK from Alkaleri; locust bean tree; dried LBP; LBPA; and concrete samples preparation in the Building Department laboratory, Modibbo Adama University, Yola are shown in Figure 1.

The ordinary Portland cement (OPC, Ashaka brand, Nigeria, specific gravity: 3.14) was used in this research. The LBP was obtained from Makurdi, Benue state, Nigeria. It was thermally digested to ash (LBPA, specific gravity: 2.18, bulk density: 875 kg/m^3 and moisture content: 1.58%) using furnace (600°C for 2 hours) and allowed to cool to room temperature before being sieved (75µm). The kaolin sample was obtained from Alkaleri (10.2713° N, 10.3301° E), Bauchi state, Nigeria. It was also thermally digested (800°C for 2 hours) to produce MK (specific gravity: 2.52, bulk density: 813 kg/m^3, and moisture content: 0.36%.), cooled to room temperature and sieved (45µm).

Figure 1. Sampling locations for LBP in Makurdi, MK from Alkaleri; locust bean tree; dried LBP; LBPA; and concrete samples preparation in Building department laboratory, Modibbo Adama University, Yola.

This figure presents the photographs of the locations where the cement replacement materials, LBP and Kaolin were sourced. It also shows photographs of locust bean tree, LBP and the LBPA produced from calcination of LBP. Additionally, the figure shows the laboratory where the experiments were conducted and concrete cast in 100mm cube steel moulds.

The chemical compositions of OPC, LBPA, and MK were determined via XRF analysis (RaynyEDX-700/800, Shimadzu Corporation, Tokyo, Japan) at Umaru Musa Yar'Adua University, Katsina, Nigeria (Table 2). The chemical compositions were silica dioxide (SiO_2), aluminium oxide (Al_2O_3), ferrous oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide

(K_2O), sulphur trioxide (SO_3), phosphorus pentoxide (P_2O_5), and titanium dioxide (TiO_2). The SiO_2 showed high percentage of concentration in OPC (19.68%), LBPA (37.03%), and MK (49.36%). OPC (60.92%) has the highest CaO content as compared to LBPA (5.1%) and MK (0.06%). MK (60.92%) has the highest Al_2O_3 content in comparison to OPC (3.33%) and LBPA (3.11%).

The chemical composition of LBPA indicates that it satisfies most requirements of ASTM C618 (2021). These include SO_3 content of 2.99%; less than the maximum of 5%, 0.08 LOI; less than 10% and 5.1% CaO, thus, a class C pozzolan. However, it has 42.81% summation of SiO_2, Al_2O_3 and Fe_2O_3; less than at least 50% requirement. In the same vein, (Ikumapayi, 2017) obtained 25% of SiO_2+ Al_2O_3+ Fe_2O_3 and (Akpenpuun et al., 2019) got 30.41%. For the MK, the result revealed that the MK conforms to the requirements of ASTM C618 (2021). Thus, MK is a Type N pozzolan having 80% summation of SiO_2, Al_2O_3, and Fe_2O_3. It also contains 0.12 % of SO_3 which is less than 5.0% required. The loss on ignition obtained was 0.12%; less 10% maximum as required for pozzolans.

Table 2. Chemical composition of OPC, LBPA, and MK.

Chemical Composition (%)	Materials		
	OPC (%)	LBPA (%)	MK (%)
SiO_2	19.68	37.03	49.36
Al_2O_3	3.33	3.11	39.37
Fe_2O_3	6.44	2.67	1.23
CaO	60.92	5.10	0.06
MgO	0.97	5.85	0.60
Na_2O	0.12	0.00	-
K_2O	0.85	9.94	0.21
SO_3	2.28	2.99	0.12
P_2O_5	0.00	3.53	0.25
TiO_2	-	-	1.71

Sand collected from Benue River in Yola, Nigeria (specific gravity: 2.67, bulk density: 1,626.04 kg/m^3 and moisture content: 2.48%) was used as fine aggregate. Crushed granite (20 mm, specific gravity: 2.70, moisture content: 1.31% and bulk density: 1883.0 kg/m^3) was used as coarse aggregate. The particle size distribution curves of both aggregates are shown in Figure 2.

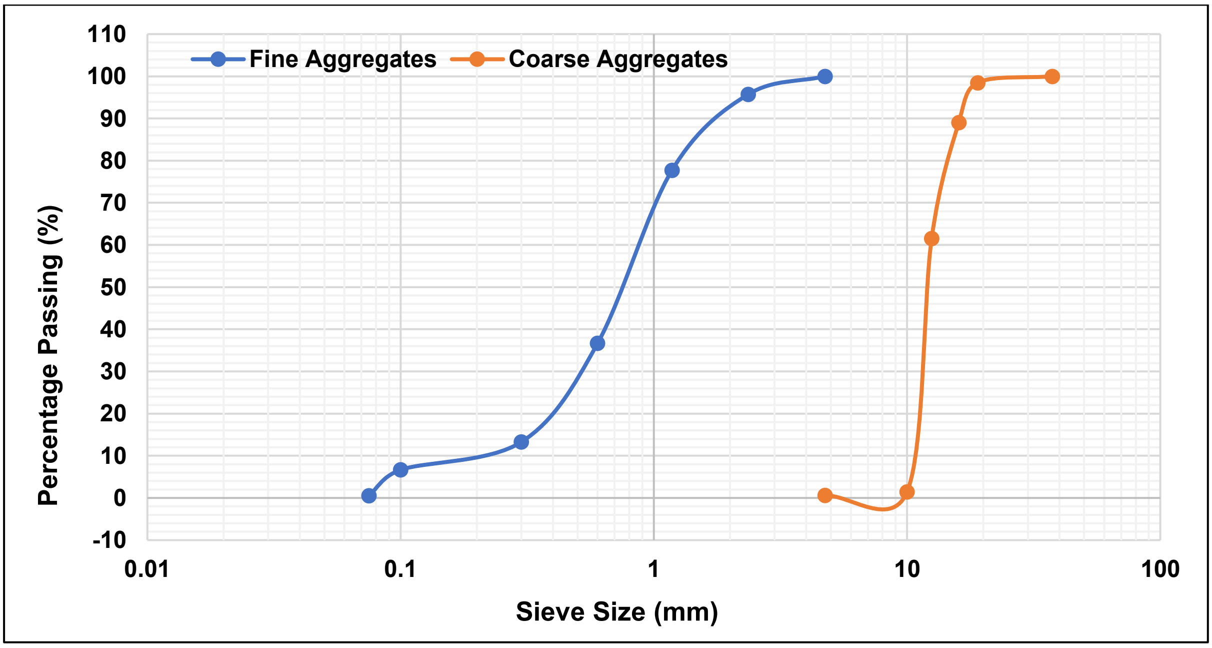

Figure 2. Particle size distribution for aggregates.

This figure presents the particle size distribution of fine and coarse aggregates plotted on a logarithmic scale. It shows fine and coarse aggregates are 4.75 and 20mm, and graded aggregates.

2.2 Concrete Mix

The mix design, workability, and setting time (s) for OPC-LBPA and OPC-LBPA-MK concrete are shown in Table 3. The LBPA as cement replacement material was evaluated (control mix (L00): 0%, L05: 5%, L10: 10%, L15: 15%, L20: 20%, L25: 25%, and L30: 30%). The combination of LBPA and MK (15%) was assessed (L05M15: 20%, L10M15: 25%, L15M15: 30%, L20M15: 35%, L25M15: 40%, and L30M15: 45%).

Workability tests (slump test and compacting factor) were performed on the fresh concrete (BS EN 12350: 2019) (BS EN 12350:2019, 2019). The slump values for OPC-LBPA concrete were 25 mm (L00), 22 mm (L05), 20 mm (L10), 18 mm (L15), 16 mm (L20), 14 mm (L25), and 12 mm (L30). The slump values for OPC-LBPA-MK concrete were 20 mm (L05M15), 19 mm (L10M15), 17 mm (L15M15), 13 mm (L20M15), 11 mm (L25M15), and 10 mm (L30M15). Both OPC-LBPA and OPC-LBPA-MK concrete showed a decrease in slump values with an increase in LBPA content (%).

The compacting factor values for OPC-LBPA concrete were 0.91 (L00), 0.88 (L05), 0.87 (L10), 0.85 (L15), 0.83 (L20), 0.81 (L25), 0.79 (L30). The compacting factor values for OPC-LBPA-MK concretes were 0.85 (L05M15), 0.80 (L10M15), 0.80 (L15M15), 0.83 (L20M15), 0.83 (L25M15), and 0.74 (L30M15). Both OPC-LBPA and OPC-LBPA-MK concrete showed a decrease in compacting factor values with an increase in LBPA content (%).

This finding is consistent with Afolayan et al. (2018). The reduction in workability may be due to the absorption of some amount of water by LBPA particles due to its large surface area. This drop in workability could also be attributed to the porous nature LBPA has due to the presence of macro and meso-pores located within and on the surface of the material which led to its huge specific surface area (Akpenpuun et al., 2019). The LBPA absorb some amount of water unto its surface during mixing causing a reduction in free water and a lower slump value (Cordeiro et al., 2012). For OPC-LBPA-MK, the slump and compacting factors further reduced on addition of MK. The results indicate a reduction in slump from 25mm of the control to 10mm for L30M15 indicating a 60% reduction. This implies that ternary systems absorb more water than control and binary concrete. The replacement of cement by MK increased water demand thus reducing the workability; MK is known to reduce concrete workability (Pillay et al., 2020). This is not only attributed to the particle size distribution of the LBPA and MK, but also to their mean particle size and geometric shape. The reduction in workability may be due to increase in the amount of silica in the MK. From the study, it was found that the silica-LBPA-MK reaction required more water in addition to water required during hydration of blends (Nwankwo & Achuenu, 2014). However, all the mixes fall within the limit for class S1 (10 mm-40 mm) specified by BS EN 206 (2013).

Setting times (initial and final) for both mix designs were recorded (BS EN 196-3, 2016). The initial and final setting times (minutes) of OPC-LBPA concrete were: L00 (85, 200), L05 (99, 238) L10 (110,250), L15 (190, 270), L20 (220, 310), L25 (226, 335), and L30 (231, 351). The initial and final setting times for OPC-LBPA-MK concrete were: L05M15 (201, 287), L10M15 (190, 301), L15M15 (191, 311), L20M15 (209, 320), L25M15 (202, 370), and L30M15 (251, 375). Both OPC-LBPA and OPC-LBPA-MK concrete showed an increase in setting times with an increase in LBPA content (%) as observed by Ja'e et al. (2019). Initial and final setting times of L05 mixtures were 17% and 19% higher than those of the control respectively. Similarly, the initial and final setting times of L30 were found to be 172% and 76% higher than those of the control samples respectively. The increase could be as a result of wider particles of LBPA and unburnt carbon (Olu et al., 2020) or its fineness (Akpenpuun et al., 2019). A comparable pattern was seen for OPC-LBPA-MK concrete. L05M15 had initial and final setting times 136% and 44% more than the control. The increase in setting times is attributed to the presence of MK in the mix which increases the setting times of concrete (Mansour & al Biajawi, 2022). The results agree with the findings of Vellaipandian (2012) who reported increase of setting times of concrete containing MK over the plain concrete. It is noteworthy that the setting time for the samples falls within the allowable limits provided by ASTM C150 (2012).

Table 3. Mix design for OPC-LBPA and OPC-LBPA-MK concrete.

Binary/ Ternary System	Mix No.	OPC (kg)	LBPA (kg)	MK (kg)	FA (kg)	CA (kg)	Water (kg)	Workability		Setting Time (s)	
								Slump (mm)	Compacting Factor	Initial	Final
Control	L00	350	-	-	700	1400	175	25	0.91	85	200
OPC-LBPA	L05	332.5	17.5	-	700	1400	175	22	0.88	99	238
	L10	315	35	-	700	1400	175	20	0.87	110	250
	L15	297.5	52.5	-	700	1400	175	18	0.85	190	270
	L20	280	70	-	700	1400	175	16	0.83	220	310
	L25	262.5	87.5	-	700	1400	175	14	0.81	226	335
	L30	245	105	-	700	1400	175	12	0.79	231	351
OPC-LBPA-MK	L05M15	280	17.5	52.5	700	1400	175	20	0.85	201	287
	L10M15	262.5	35	52.5	700	1400	175	19	0.80	190	301
	L15M15	245	5.5	52.5	700	1400	175	17	0.83	191	311
	L20M15	227.5	70	52.5	700	1400	175	13	0.83	209	320
	L25M15	210	87.5	52.5	700	1400	175	11	0.80	202	370
	L30M15	192.5	105	52.5	700	1400	175	10	0.74	251	375

2.3 Strength Properties

2.3.1 Compressive Strength

Compressive strength test was performed on the concrete (BS EN 12390-4, 2019). The samples were cast in 100 mm steel cube moulds and cured in water (3, 7, 14, 28, 56 and 90 days). 234 cubes were cast and three samples were crushed at the conclusion of each curing procedure using the Civit Test Hydraulic Universal Testing Machine of 1000 kN capacity and at constant rate of 15 kN/s and the average taken.

2.3.2 Flexural Strength

Flexural strength test was performed on the concrete (BS EN 12390-5, 2019). Mixing was done manually and the concrete cast in steel beam moulds (150 x 150 x 750mm long) and kept in water (3,7,14,28,56, and 90 days).

2.3.4 Tensile Strength

Splitting tensile strength was determined (BS EN 12390-6, 2009). Mixing was done manually and cast in steel cylindrical moulds of 150mm diameter by 300mm long and cured in water (3, 7, 14, 28,56 and 90 days).

2.5 Extreme pH Resistance

Chemical attacks severely affect concrete durability (Budiea et al., 2022). Concrete is alkaline in nature due to the presence of Calcium Hydroxide {$Ca(OH)_2$} which reacts with acids to lower the degree of alkalinity (Manjeeth & Rama, 2015). The effects of extreme pH on LBPA concrete are have not been studied. Hence the concrete was tested in hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) (Patil & Patel, 2022) and sulphate solutions.

2.5.1 Acid

The cubes were cast and cured in water at 25 ± 2˚C (28 days). Thereafter, the samples were air dried and immersed in 5% concentration of HCl and H_2SO_4 (Acharya & Patro, 2016; Koushkbaghi et al., 2019). The cubes were removed from the acid solutions at 7 days' interval until the 28th day to determine the compressive strength of the samples after the acid degradation.

2.5.2 Sulphate

The cubes were cured in water at room temperature (28 days). The sample cubes were thereafter soaked in 10% sodium sulphate solution. The samples were tested for compressive strength at 7 days interval until the 28th day.

2.6. Model Optimization

Model optimization was conducted using I-Optimal design with second order polynomial equation (Eq. 1) in RSM using the Design Expert ® software (Version 12). The optimization is required to assess the link between process variable, LBPA composition in concrete (%) (control mix, OPC-LBPA, and OPC-LBPA-MK) with the response variables (compressive strength, split tensile strength, flexural strength, extreme pH resistance).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot x_i + \sum_{i=1}^{k} \beta_{ii} \cdot x_i^2 + \cdots + \sum_{i \le j}^{k} \sum_{j}^{k} \beta_{ij} \cdot x_i \cdot x_i + \cdots + e \quad (1)$$

$Y =$ $Predicted\ response\ variable\ (Strengths\ (compressive, split\ tensile, flexural),\ extreme\ pH\ resistance)$
$\beta =$ Regression coefficient
$x_i = Linear\ term\ for\ variable\ 1\ (Percentages\ of\ BA)$
$x_i^2 = Nonlinear\ squared\ term\ for\ variable\ 1\ (Percentages\ of\ LBPA)$
$x_i^3 = Nonlinear\ squared\ term\ for\ variable\ 1\ (Percentages\ of\ LBPA)$
$x_i^4 = Nonlinear\ squared\ term\ for\ variable\ 1\ (Percentages\ of\ LBPA)$
$x_i^5 = Nonlinear\ squared\ term\ for\ variable\ 1\ (Percentages\ of\ LBPA)$
$x_i^6 = Nonlinear\ squared\ term\ for\ variable\ 1\ (Percentages\ of\ LBPA)$
$k =$ Number of factors or process variables in the experiment
$e =$ Random error

The percentages of error between experimental and predicted values of response variables were evaluated using Eq. 2.

$$Error\ (\%) = \left| \frac{Experimental\ Value - Predicted\ Value}{Experimental\ Value} \times 100\% \right| \quad (2)$$

The ranges of process (OPC-LBPA (%) and OPC-LBPA-MK (%)) and response variables (OPC-LBPA: HCl (N/mm^2), OPC-LBPA:H_2SO_4 (N/mm^2), OPC-LBPA: Sulphate (N/mm^2), OPC-LBPA-MK: HCl (N/mm^2), OPC-LBPA-MK: H_2SO_4 (N/mm^2), and OPC-LBPA-MK: Sulphate (N/mm^2) are shown in Table 4.

Table 4. Process and response variables.

Design Type	Mix Design			Coded Factors	Units	Analysis	Low Actual	High Actual	Mean	Standard Deviation	Model
I-Optimal Design	HCl	Process Variable	Mix Design OPC-LBPA	A	%	-	5 (-1)	15 (+1)	9.79	3.65	-
		Response Variables	Compressive Strength LBPA		N/mm^2	Polynomial	11.2 (-1)	22.1 (+1)	14.80	4.63	Sixth
			Compressive Strength LBPA-MK		N/mm^2	Polynomial	24.1 (-1)	27.3 (+1)	25.61	1.20	Sixth
	H_2SO_4	Process Variable	Mix Design OPC-LBPA		%	-	5 (-1)	20 (+1)	12.78	5.47	-
		Response Variables	Compressive Strength LBPA		N/mm^2	Polynomial	10 (-1)	18.2 (+1)	12.82	2.90	Sixth
			Compressive Strength LBPA-MK		N/mm^2	Polynomial	13.7 (-1)	24.5 (+1)	18.40	4.39	Fifth
		Process Variable	Mix Design OPC-LBPA		%	-	5 (-1)	20 (+1)	12.83	5.49	-

	Sulphate	Response Variables	Compressive Strength LBPA		N/mm^2	Polynomial	10.5 (-1)	21.3 (+1)	15.83	4.13	Sixth
		Process Variable	Mix Design OPC-LBPA		%	-	15 (-1)	30 (+1)	22.18	5.50	-
		Response Variables	Compressive Strength LBPA-MK		N/mm^2	Polynomial	12.9 (-1)	25 (+1)	19.41	4.28	Fifth

III. RESULTS AND DISCUSSION

3.1 Strength Properties

3.1.1 Compressive Strength

Figure 3 is the result of compressive strength of OPC-LBPA and OPC-LBPA-MK concrete. The compressive strength improved with age of curing but decreased with increase in LBPA content. The drop in compressive strength is because of drop in workability with increase in LBPA content as fresh properties of concrete affect hardened properties (Mindess et al., 2003). The study also observed that the control samples had greater early strength than the OPC-LBPA samples. The slow rate of strength development is due to the presence of LBPA in the concrete; pozzolans are known to reduce the early strength of concrete due to slow rate of hydration (Ahmed, 2019). The 28-day compressive strength of OPC-LBPA concrete ranged from 44.3 – 96.1 % of control with least compressive strength at 30% LBPA content. It was however observed that the 28-day compressive strength of L10 is marginally lower than that of control. The LBPA reduced the amount of cement in the mix that was available for the hydration process, which in turn decreased the formation of the stable strength-producing cementitious compounds (Ogork et al., 2014). However, at 56 and 90 days, the control samples showed little increase in strength compared to the OPC-LBPA concrete with L05 having higher strength than the control. The difference in strength gains between the OPC-LBPA concrete and the control is because LBPA content present in the matrix improves the properties of concrete at the later age of curing(Neville & Brooks, 2010). This result also agrees with the findings of (Aquino et al., 2001) and (Ahmadi et al., 2007) who stated that pozzolan mixes develop higher strength at later age of curing.

For the OPC-LBPA-MK concrete, 5, 10, 15 and 20% LBPA combined with 15% MK replacement had better early strength than the control with L10M15 having the highest compressive strength at 3 days curing. In all cases, the compressive strength increased with curing age. At 28 days, L05M15, L10M15 and L15M15 had compressive strength greater than that of the control concrete. This improvement in strength is attributed to the synergy between the less reactive LBPA and more reactive MK (Isaia, 1999). The pozzolanic interaction between MK and $Ca(OH)_2$, which results in the creation of more C-S-H gel, can also be linked to the improved strength qualities. The considerably smaller MK particles fill the gaps between the OPC and LBPA particles thanks to the comparable properties that MK possesses as a filler material (Pillay et al., 2020). It was also observed that there was a drastic loss of strength after 14 days of curing for L30M15. This is because higher quantity of LBPA outperformed the MK in the mix leading to reduction in synergic reaction, hence the loss of strength. The reduction in compressive strength may also be due to clinker dilution effect (Ramezanianpour and Bahrami, 2012).

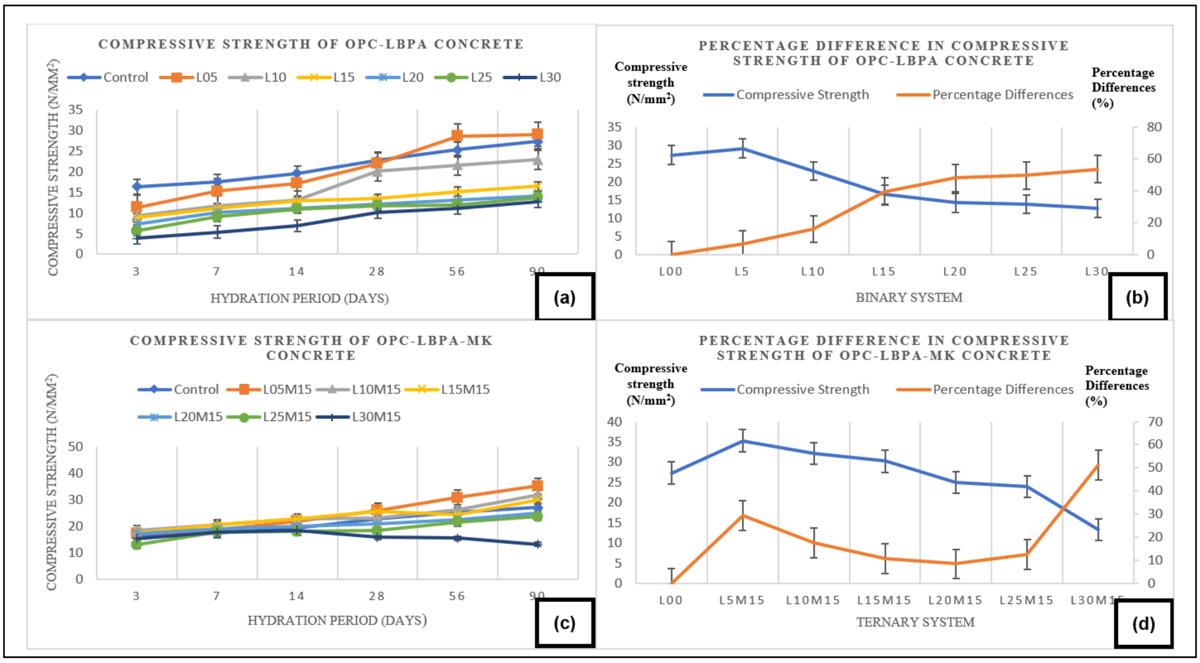

Figure 3. Compressive strength of OPC-LBPA concrete (a), percentage difference in compressive strength of OPC-LBPA concrete (b), compressive strength of OPC-LBPA-MK concrete (c), and percentage difference in compressive strength of OPC-LBPA-MK concrete (d).

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the compressive strength of concrete while the right axis represents the percentage change in compressive strength the of concrete. Concrete strength increased with an increase in curing time and decreased with increase in LBPA content.

3.1.2 Flexural Strength

The flexural strength behaviour of OPC-LBPA and OPC-LBPA-Mk concrete is similar to that of compressive strength (Figure 4). The result indicates that flexural strength increased with curing age but decreased with increase in LBPA consistent with (Auta et al., 2020; Olubajo et al., 2020). The flexural strength of control samples was higher than that of LBPA concrete at 28 days. However, the flexural strength of L05 concrete was greater than that of the control samples at 56 and 90 days of curing. The lower flexural strength of LBPA concrete would be attributed to low pozzolanic reaction of LBPA. The flexural strength of OPC-LBPA-MK concrete increased with curing age but decreased with increase in combined LBPA-MK content beyond 25%. The result shows that inclusion of MK in the mix enhanced the flexural strength of the OPC-LBPA-MK concrete. The enhancement in at low level of LBPA-MK substitution may be due to increased pozzolanic reaction and the packing ability of the fine particles of MK (Siddique & Klaus, 2009). The decrease in flexural strength with increase LBPA-MK content maybe attributed to dilution effect of OPC and weaker formation of C-S-H gel as a result of pozzolanic reaction of LBPA-MK (Prasanphan et al., 2010).

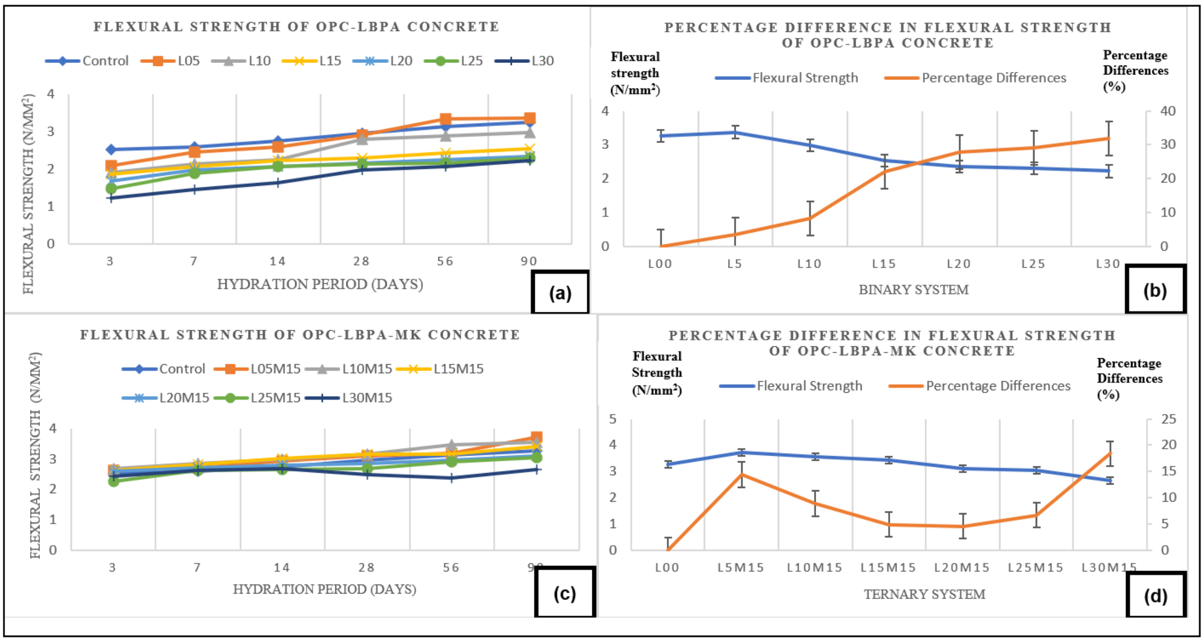

Figure 4. Flexural Strength of OPC-LBPA concrete (a), percentage difference in compressive strength of OPC-LBPA concrete (b), flexural strength of OPC-LBPA-MK Concrete (c), and percentage difference in OPC-LBPA-MK concrete (d).

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the flexural strength of concrete while the right axis represents the percentage change in flexural strength the of concrete. Flexural strength increased with an increase in curing time and decreased with increase in LBPA content.

3.1.3 Splitting Tensile Strength

The splitting tensile strength increased with curing age but decreased with increase in LBPA content for OPC-LBPA concrete. It was observed that the tensile strength of control sample was higher than that of the LBPA concrete at 28 days in line with (Yalley, 2019). However, the tensile strength of L05 concrete was greater than that of the control sample at 56 and 90 days of curing. The 28 tensile strength of control sample was 2.65 N/mm^2 whereas that of OPC-LBPA concrete ranged from 72.83 to 98.11% of control with concrete containing 5% and 30% LBPA content having the maximum and minimum strengths, respectively. The splitting tensile strength of OPC-LBPA-MK concretes increased with curing age but decreases with increase in percentage of combined LBPA-MK content beyond 25% combined replacement level. The tensile strengths of OPC-LBPA-MK were higher than that of the control and binary samples for all ages. The enhancement in tensile strength at low level of LBPA-MK substitution may be due to increased pozzolanic reaction and the packing ability of the fine particles of MK (Siddique & Klaus, 2009).

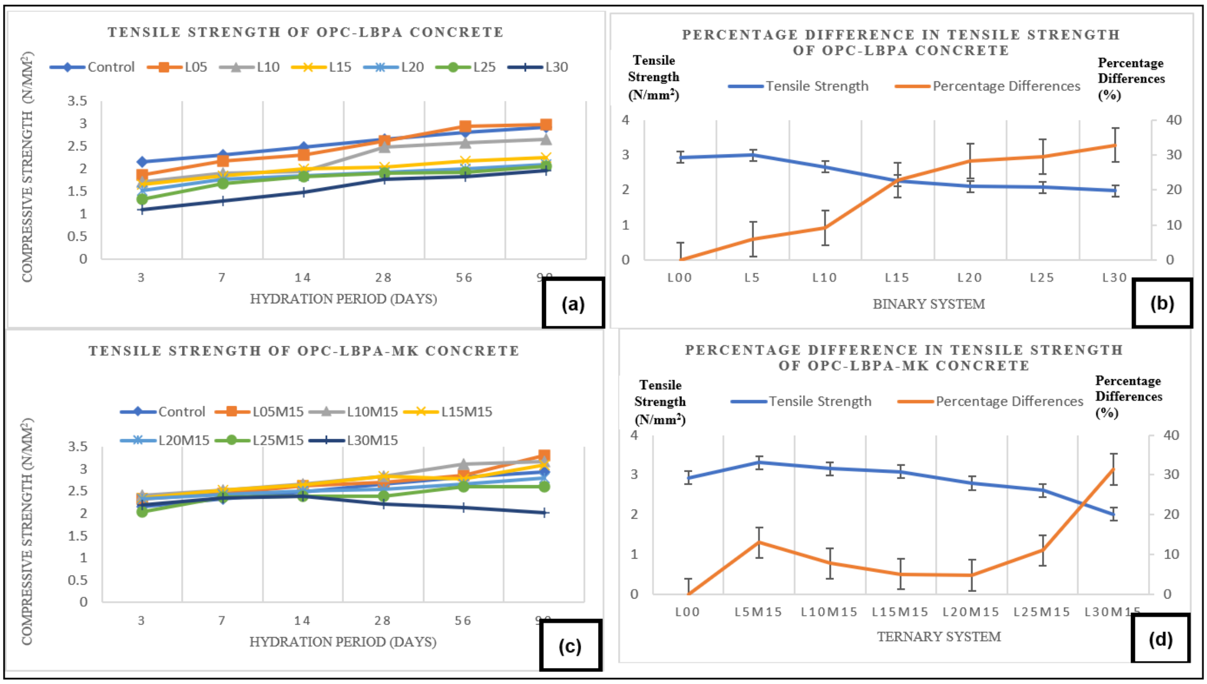

Figure 5. Tensile strength of OPC-LBPA concrete (a), percentage difference in tensile strength of OPC-LBPA concrete (b), tensile strength of OPC-LBPA-MK concrete (c), and percentage difference in tensile strength of OPC-LBPA-MK concrete(d)

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the tensile strength of concrete while the right axis represents the percentage change in tensile strength the of concrete. Tensile strength increased with an increase in curing time and decreased with increase in LBPA content.

3.2 Extreme pH Resistance

3.2.1 Acid

Figures 6 and 7 are the graphs of compressive strength of LBPA concrete subjected to acid attacks. The effect of 5% concentration of HCl and H_2SO_4 acids on LBPA concrete's compressive strength showed the compressive strength declined drastically at 7 days of immersion in acids but increased from 14 days onward. LBPA concrete offered better resistance to deterioration by HCl than control, while control concrete performed marginally better than LBPA concrete in H_2SO_4. While there was a 10.96% loss of compressive strength of the control concrete, L05 gained 0.91% compressive strength after 28 days of immersion in HCl. The percentage loss in compressive strength for L00 and L05 in H_2SO_4 acid were 17.54 % and 16.89 %, respectively. It is possible that the LBPA pozzolanic reaction depleted the $Ca(OH)_2$ content of the concrete, leaving less $Ca(OH)_2$ accessible to react with HCl acid, or that the LBA concrete had less C_3A available to create the more disruptive ettringite (Zivica & Bajza, 2001). This explains why, despite the fact that HCl acid is a very potent acid, LBPA concrete has better resistance to it. OPC-LBPA-MK has further improved performance against both acids. The L05M15 and L10M15 gained 5 and 3.4% and lost 5.8 and 3.4% in HCl and H_2SO_4 acid respectively.

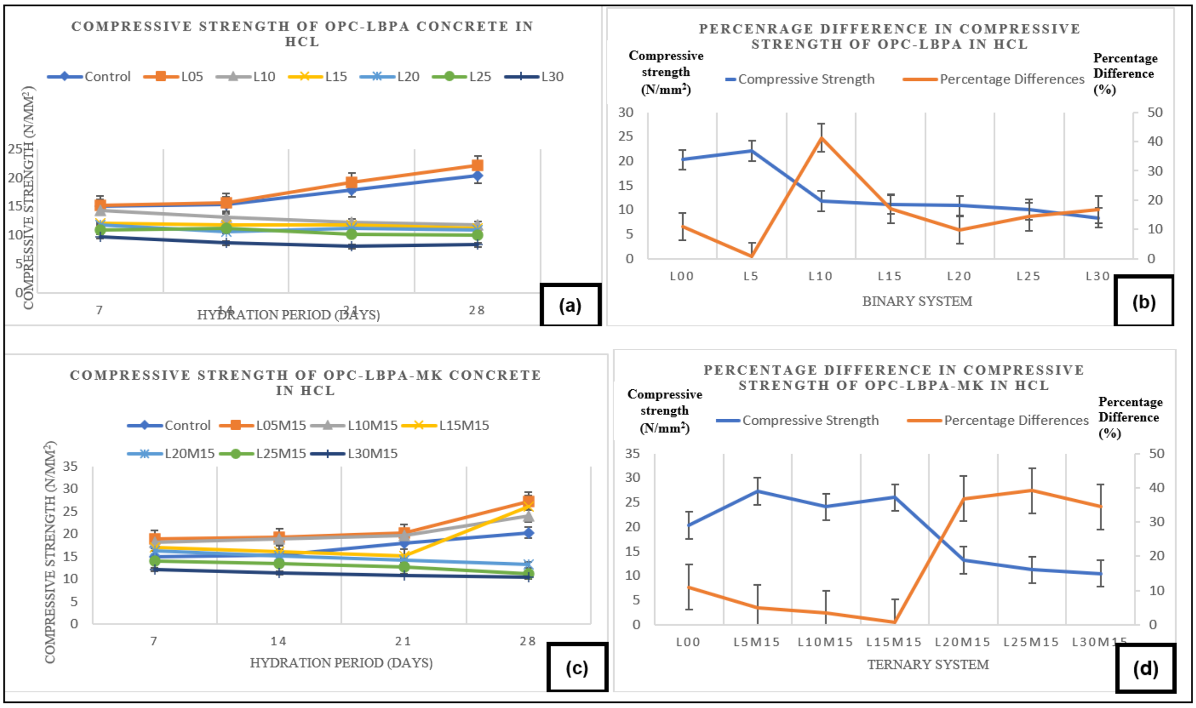

Figure 6. Compressive Strength of OPC-LBPA (a), percentage change in compressive strength of OPC-LBPA-MK (b), compressive strength of OPC-LBPA-MK (c), and percentage change in compressive strength of OPC-LBPA-MK Concrete (d) immersed in HCl Acid Solution.

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the compressive strength of concrete while the right axis represents the percentage change in compressive strength the of concrete after HCl degradation. The strength decreases with an increase in immersion time and LBPA content and the strength was regained after 28 days.

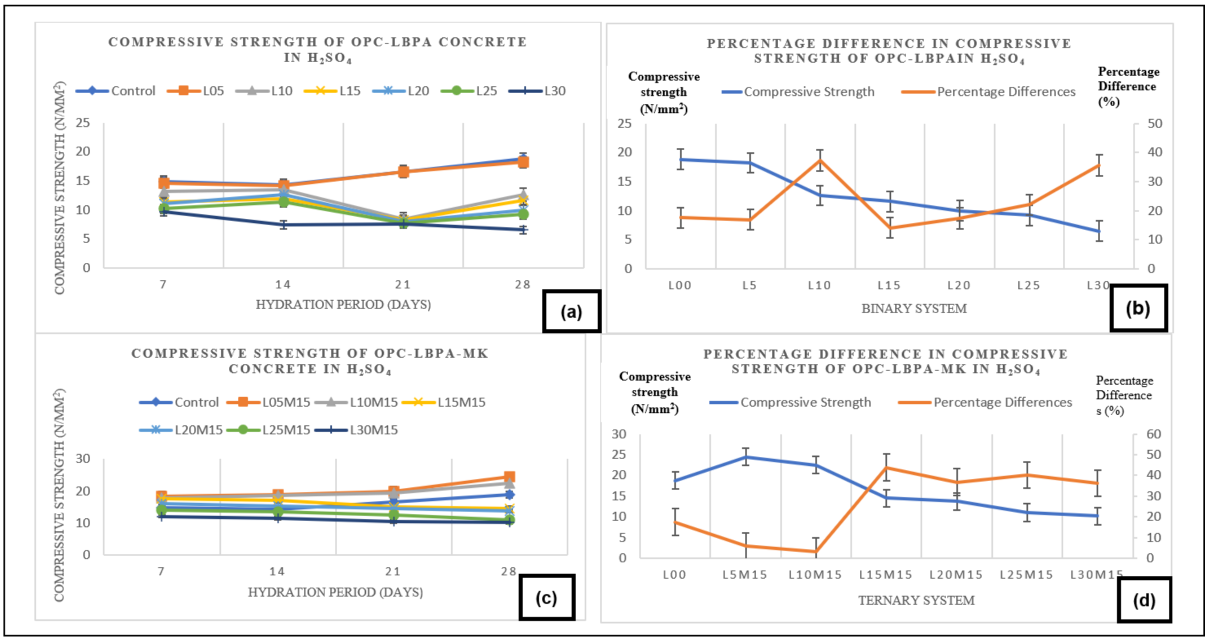

Figure 7. Compressive Strength of OPC-LBPA (a), percentage difference in compressive strength of OPC-LBPA (b), compressive strength of OPC-LBPA-MK (c), and percentage difference in compressive strength of OPC-LBPA-MK concrete immersed in H_2SO_4 Acid Solution.

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the compressive strength of concrete while the right axis represents the percentage change in compressive strength the of concrete after H_2SO_4 degradation. The strength decreases with an increase in immersion time and LBPA content; regained after 28 days.

3.2.2 Sulphate

The OPC-LBPA concrete has better resistance to Sodium Sulphate (Na_2SO_4) than the control concrete (Figure 8) with L05 exhibiting the highest resistance. The compressive strength decreased by 11%, 2.7%, 5.0% and 16% for L00, L05, L10 and L30 respectively after 28 days' immersion. The resistance may be attributed to the silicate gel produced during hydration processes which coats and binds matrix together and to block off the Sulphate action in the concrete structure (Yalley, 2019). Another reason could be that the pozzolanic reaction from LBPA produces additional binding gel that forms a more compact concrete. The pozzolanic reaction have consumed calcium hydroxide which could have been transformed into ettringite that eventually affected the concrete (Muthusamy *et al.*, 2022). For OPC-LBPA-MK concrete, the resistance improved with inclusion of MK. The strength of L05M15, L10M15 and L15M15 reduced by 1.9, 2.6 and 3.1% respectively at 28 days after initial decline of at 7 days. The improved resistance is attributed to the presence of MK which is known to improve the resistance of concrete against sulfate attacks. This is because pozzolans are known to enhance concrete's resistance against Sulphate attack (Ahmad et al., 2020).

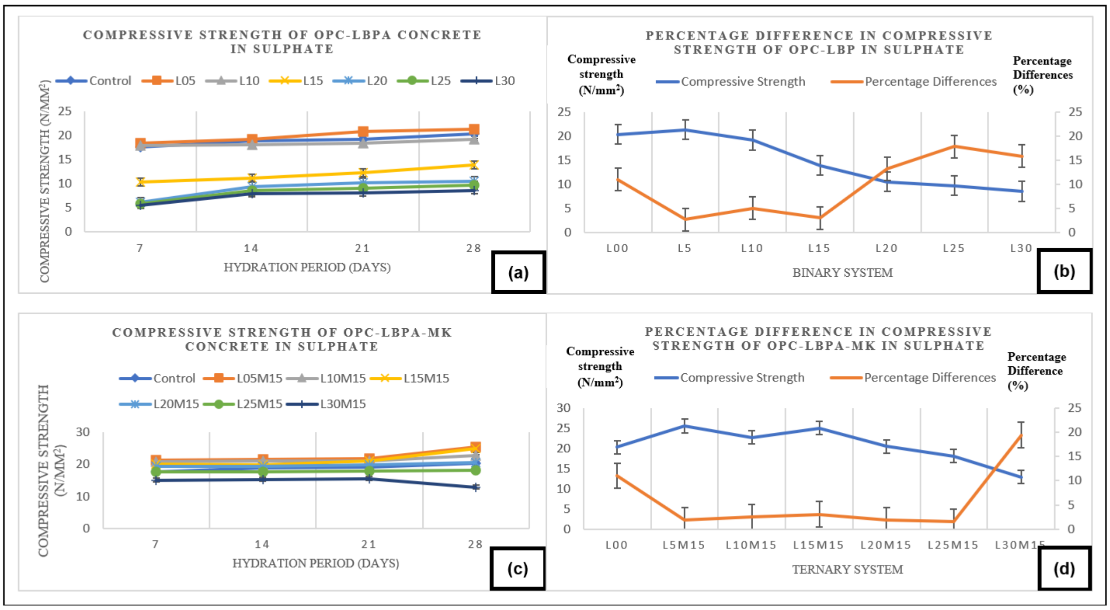

Figure 8. Compressive Strength of OPC-LBPA (a), percentage difference in compressive strength of OPC-LBPA (b), compressive strength of OPC-LBPA-MK (c) and percentage difference in compressive strength of OPC-LBPA-MK concrete immersed in Na_2SO_4 Solution.

This figure shows two uniaxial and two bi-axial line graphs with the left axis and the lines representing the compressive strength of concrete while the right axis represents the percentage change in compressive strength the of concrete after sodium sulphate degradation. The strength decreases with an increase in immersion time and LBPA content.

3.4 Model Optimization

The design layout in (RSM) is shown in Table 5. The 13 experimental runs in the RSM optimization, consisting of process (% of LBPA and LBPA-MK) and response variables to extreme pH (HCl, H_2SO_4 and Sulphate) were carried out using I-Optimal design. The value of responses for the missing LBPA and MK percentages were interpolated within ranges of 0 to 30% for LBPA and 15% for MK from Figs. 3, 6, 7 and 8. The analysis of variance (Anova) for response variables for OPC-LBPA: HCl (sixth model), OPC-LBPA: H_2SO_4 (sixth model), OPC-LBPA: Sulphate (sixth model), OPC-LBPA-MK: HCl (sixth model), OPC-LBPA-MK: H_2SO_4 (fifth model), OPC-LBPA-MK: Sulphate (fifth model) is shown in Table 6. Model terms for every model with any values of Prob > F< 0.05) are classified as significant.

Table 5. Design layout in RSM

Run	Process Variable	Response Variable Compressive Strengths (N/mm^2) under Extreme pH-HCl	
	Mix Design	OPC-LBPA	OPC-LBPA-MK
1.	10	11.8	24.1
2.	11.2302	11.678	24.48
3.	15	11.2	26
4.	5	22.1	27.3
5.	5	22.1	27.3
6.	5	22.1	27.3
7.	10	11.8	24.1
8.	8.3	15.92	25.38
9.	6.6	17.98	26.02
10.	12.45	11.434	25.24
11.	10	11.8	24.1
12.	13.7	11.312	25.62
13.	15	11.2	26

Run	Process Variable	Response Variable Compressive Strengths (N/mm^2) under Extreme pH-H_2SO_4	
	Mix Design	OPC-LBPA	OPC-LBPA-MK
1.	10.625	12.4	20.9
2.	17.45	10.64	14.02
3.	12.5	12	17.7
4.	8.75	13.72	22.9
5.	12.5	12	17.7
6.	5	18.2	24.5
7.	20	10	13.7
8.	20	10	13.7
9.	12.5	12	17.7
10.	5	18.2	24.5
11.	20	10	13.7
12.	14.9	11.6	14.5
13.	6.95	15.96	23.7

Run	Process Variable	Response Variable Compressive Strengths (N/mm^2) under Extreme pH-Sulfate	
	Mix Design	OPC-LBPA	OPC-LBPA-MK
1.	10.655	18.06	18.58
2.	8.825	19.54	23.2
3.	6.95	20.42	17.06
4.	20	10.5	25
5.	12.5	15.98	20.5
6.	20	10.5	19.06
7.	5	21.3	12.9
8.	5	21.3	19.06
9.	17.75	11.86	14.98
10.	12.5	15.98	19.06

11.	15.2	13.9	25
12.	20	10.5	25
13.	12.5	15.98	12.9

Table 6. Analysis of variance (Anova) for response variables such as HCL, H_2SO_4 and Sulphate.

Response Variables for OPC - LBP A	Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Indication	Response Variables for OPC - LBP A-MK	Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Indication
HCl	Model	257.03	6	42.84	688.51	< 0.0001	significant	HCl	Model	17.34	6	2.89	1560.08	< 0.0001	Significant
	A-Mix Design L	6.26	1	6.26	100.69	< 0.0001	significant		A-Mix Design LM	0.183	1	0.183	98.8	< 0.0001	significant
	A^2	3.87	1	3.87	62.17	0.0002	significant		A^2	1.13	1	1.13	610	< 0.0001	significant
	A^3	0.6485	1	0.6485	10.42	0.0179	significant		A^3	0.0957	1	0.0957	51.67	0.0004	significant
	A^4	1.89	1	1.89	30.34	0.0015	significant		A^4	0.476	1	0.476	257.01	< 0.0001	significant
	A^5	0.6899	1	0.6899	11.09	0.0158	significant		A^5	0.112	1	0.112	60.48	0.0002	significant
	A^6	1.64	1	1.64	26.33	0.0022	significant		A^6	0.3761	1	0.3761	203.07	< 0.0001	Significant
	Residual	0.3733	6	0.0622					Residual	0.0111	6	0.0019			
	Lack of Fit	0.3733	1	0.3733					Lack of Fit	0.0111	1	0.0111			
	Pure Error	0	5	0					Pure Error	0	5	0			
	Cor Total	257.4	12						Cor Total	17.35	12				

	Model	100.85	6	16.81	1.28E+05	< 0.0001	significant		Model	231.13	5	46.23	27746.45	< 0.0001	Significant

H_2SO_4	A-Mix Design L	0.093	1	0.093	706.16	< 0.0001	significant	H_2SO_4	A-Mix Design LM	19.03	1	19.03	11420.54	< 0.0001	Significant
	A^2	0.0125	1	0.0125	94.61	< 0.0001	significant		A^2	1.01	1	1.01	608.93	< 0.0001	Significant
	A^3	0.4536	1	0.4536	3442.4	< 0.0001	significant		A^3	2.38	1	2.38	1430.04	< 0.0001	Significant
	A^4	0.0107	1	0.0107	80.83	0.0001	significant		A^4	0.3831	1	0.3831	229.96	< 0.0001	Significant
	A^5	0.2684	1	0.2684	2036.91	< 0.0001	significant		A^5	1.3	1	1.3	781.62	< 0.0001	Significant
	A^6	0.0101	1	0.0101	76.41	0.0001	significant		Residual	0.0117	7	0.0017			
	Residual	0.0008	6	0.0001					Lack of Fit	0.0117	2	0.0058			
	Lack of Fit	0.0008	1	0.0008					Pure Error	0	5	0			
	Pure Error	0	5	0					Cor Total	231.14	12				
	Cor Total	100.85	12												

Sulphate	Model	204.4	6	34.07	7698.31	< 0.0001	significant	Sulphate	Model	220.23	5	44.05	10415.02	< 0.0001	Significant
	A-Mix Design L	6.27	1	6.27	1416.31	< 0.0001	significant		A-Mix Design LM	0.6219	1	0.6219	147.06	< 0.0001	Significant
	A^2	0.1725	1	0.1725	38.97	0.0008	significant		A^2	0.1523	1	0.1523	36.02	0.0005	Significant
	A^3	0.0839	1	0.0839	18.96	0.0048	significant		A^3	0.914	1	0.914	216.13	< 0.0001	Significant
	A^4	0.1638	1	0.1638	37.01	0.0009	significant		A^4	0.2138	1	0.2138	50.55	0.0002	Significant
	A^5	0.0226	1	0.0226	5.1	0.0647	Not significant		A^5	0.6078	1	0.6078	143.72	< 0.0001	Significant
	A^6	0.1434	1	0.1434	32.39	0.0013	significant		Residual	0.0296	7	0.0042			

	Residual	0.0266	6	0.0044					Lack of Fit	0.0296	2	0.0148			
	Lack of Fit	0.0266	1	0.0266					Pure Error	0	5	0			
	Pure Error	0	5	0					Cor Total	220.26	12				
	Cor Total	204.43	12												

The significant regression parameters of predictive models in terms of actual factors are shown in Eq. 3 (OPC-LBPA: HCl), 4 (OPC-LBPA: H_2SO_4), 5 (OPC-LBPA: Sulphate), 6 (OPC-LBPA-MK: HCl), 7 (OPC-LBPA-MK: H_2SO_4) and 8 (OPC-LBPA-MK: Sulphate). Generally, the quadratic models are significant for the optimization purpose (Table 7).

The R^2 (OPC-LBPA; HCl: 0.9985, OPC-LBPA; H_2SO_4: 0.9999, OPC-LBPA; Sulphate: 0.9999, OPC-LBPA-MK; HCl: 0.9994, OPC-LBPA-MK; H_2SO_4: 0.9999, OPC-LBPA-MK; Sulphate: 0.9999) represents goodness of fit close to 1 (Gauthier & Hawley, 2015; Manan et al., 2021).

$$Compressive\ strength\ LBPA_{HCl} = 1204.97701 - 801.17885A + 219.34436A^2 - 31.10359A^3 + 2.40746A^4 - 0.096609A^5 + 0.001574A^6 \tag{3}$$

$$Compressive\ strength\ LBPA_{H2SO4} = -25.87152 + 27.44732A - 6.29805A^2 + 0.678726A^3 - 0.037874A^4 + 0.001055A^5 - 0.000012A^6 \tag{4}$$

$$Compressive\ strength\ LBPA_{Sulphate} = 103.52518 - 49.23819A + 11.67377A^2 - 1.40415A^3 + 0.089957A^4 - 0.002938A^5 + 0.000039A^6 \tag{5}$$

$$Compressive\ strength\ LBPA\ MK_{HCl} = 571.79426 - 372.44401A^2 + 102.85269A^3 - 1.14398A^4 - 0.046129A^5 + 0.000754A^6 \tag{6}$$

$$Compressive\ strength\ LBPA\ MK_{H2SO4} = 75.86803 - 27.71691A + 5.64326A^2 - 0.539962A^3 + 0.0237610.1A^4 - 0.000390.1A^5 \tag{7}$$

$$Compressive\ strength\ LBPA\ MK_{Sulphate} = -1276.80796 + 309.27329A - 28.71292A^2 + 1.30398A^3 - 0.029056A^4 - 0.000254A^5 \tag{8}$$

Table 7. Fit summary results for OPC-LBPA and OPC-LBPA-MK.

Mix Design	Significant model	Std. Dev.	R^2	Adj. R^2	Predicted R^2	Adeq. Precision
OPC-LBPA	HCl	0.2494	0.9985	0.9971	0.4972	59.5248
	H_2SO_4	0.0115	0.9999	0.9999	0.9973	973.4588
	Sulphate	0.06652	0.9999	0.9997	0.9567	221.3017
OPC-LBPA-MK	HCl	0.0430	0.9994	0.9987	0.7779	100.7120
	H_2SO_4	0.04082	0.9999	0.9999	0.9997	389.5569
	Sulphate	0.06503	0.9999	0.9998	0.9994	273.8104

The β coefficient of actual factors for compressive strength for OPC-LBPA: HCl sixth model and its model terms are 1204.97701 (y-intercept), -801.17885 (A), 219.34436 (A^2), -31.10359 (A^3), 2.40746 (A^4), 0.096609 (A^5) and 0.001574 (A^6). Quadratic model compressive strength and model terms A^2, A^3, A^4, A^5 and A^6 are significant (P-value < 0.05). The β coefficient of actual factors for compressive strength for OPC-LBPA:H_2SO_4 sixth model and its model terms for actual factors are −25.87152 (y-intercept), 27.44732 (A), −6.29805 (A^2), 0.678726 (A^3), −0.037874 (A^4), 0.001055 (A^5) and – 0.00012 (A^6). Quadratic model compressive strength and model terms A^2, A^3, A^4, A^5 and A^6 are significant (P-value < 0.05). The β coefficient of actual factors for compressive strength sixth model for OPC-LBPA: Sulfate, and its model terms for actual factors are 103.52518 (y-intercept), − 49.23819 (A), 11.67377 (A^2), − 1.40415 (A^3) 0.089957 (A^4), − 0.002938 (A^5) and 0.00039 (A^6). Quadratic model compressive strength and model terms A^2, A^3, A^4 and A^6 are significant (P-value < 0.05). The β coefficient of actual factors for compressive strength sixth model for OPC-LBPA-MK: HCl and its model terms for actual factors are 571.79426 (y-intercept), − 372.44401 (A^2), 102.85269 (A^3) −1.14398 (A^4), − 0.046129 (A^5) and 0.000754 (A^6). Quadratic model compressive strength and model terms A^2, A^3, A^4, A^5 and A^6 are significant (P-value < 0.05). The β coefficient of actual factors for compressive strength sixth model for LBPA-MK: H_2SO_4 and its model terms for actual factors are 75.86803 (y-intercept), −27.71691 (A), 5.64326 (A^2), − 0.539962 (A^3), 0.02376101 (A^4), and – 0.0003901 (A^5). Quadratic model terms A^2, A^3, A^4 and A^5 are significant (P-value < 0.05). The β coefficient of actual factors for compressive strength sixth model for OPC-LBPA-MK: Sulphate and its model terms for actual factors are -1276.80796 (y-intercept), 309.27329 (A), − 28.71292 (A^2), 1.30398 (A^3), − 0.029056(A^4) and – 0.000254 (A^5). Quadratic model compressive strength and model terms A^2, A^3 A^4, and A^5 are significant (P-value < 0.05).

The patterns of predicted versus actual values plot is shown in Fig. 9. The scatterplots of Predicted vs. actual values plot for a. OPC-LBPA: HCl, b. OPC-LBPA: H_2SO_4, c. OPC-LBPA: Sulphate, d. OPC-LBPA-MK: HCl, e. OPC-LBPA-MK: H_2SO_4, f. OPC-LBPA-MK: Sulphate were in a straight line showing a linear relationship and the proposed model terms were sufficient, and constant variance assumption was verified.

The 2-D plots for a. OPC-LBPA: HCl, b. OPC-LBPA: H_2SO_4, c. OPC-LBPA: Sulphate, d. OPC-LBPA-MK: HCl, e. OPC-LBPA-MK: H_2SO_4, f. OPC-LBPA-MK: Sulphate are shown in Fig. 10. Fig. 10a shows that 5% (run 5) and 8.3% (run 8) of OPC-LBPA has predicted compressive strength of 22.1 and 15.92 N/mm^2 in HCl respectively. At 10% (run 1), 12.45% (run 10), 13.7% (run 12), and 15% (run 13) of OPC-LBPA had estimated 11.8, 11.434, 11.312, and 11.2 N/mm^2 of compressive strength correspondingly. Fig. 10b shows that 5% (run 5) and 6.95% (run 13) of OPC-LBPA had predicted compressive strength of 18.2 and 15.96 N/mm^2 in H_2SO_4 respectively. At 8.75% (run 4), 12.5% (run 10), 14.9% (run 12), 17.45 (run 2) and 20% (run 7) of OPC-LBPA had estimated 13.72, 12.0, 11.6, 10.64, and 10.0 N/mm^2 of compressive strength correspondingly. Fig. 10c shows that 5% (run 7) and 6.95% (run 3) of OPC-LBPA has predicted compressive strength of 21.3 and 20.42 N/mm^2 in Sulphate. At 8.825% (run 2), 12.5% (run 13), 15.2% (run 4), 17.75% (run 2), and 20% (run 12) of OPC-LBPA had estimated 19.54, 15.98, 13.9, 11.86, and 10.5 N/mm^2 of compressive strength respectively. Fig. 10d shows that 5% (run 6) and 6.6% (run 9) of OPC-LBPA-MK have predicted compressive strength of 27.3 and 26.02 N/mm^2 in HCl. At 8.3% (run 8), 10% (run 1), and 11.2302% (run 2), the estimated strengths are 25.38, 24.1 and 24.48 respectively. At 12.45% (run 10), 13.7% (run 12) and 15% (run 13) the predicted strengths are: 125.24, 25.62, and 26.0 N/mm^2 respectively. Fig. 12e shows that 5% (run 6) and 6.95% (run 9) of OPC-LBPA-MK has predicted compressive strength of 24.5 and 23.7 N/mm^2 in H_2SO_4. At 8.75% (run 4), 10.625% (run 1), and 12.5% (run 5), the estimated strengths are 22.9, 20.9 and 17.7 respectively. At 14.9% (run 12), 17.45% (run 10) and 20% (run 7) the predicted strengths are: 14.5, 14.02, and 13.7 N/mm^2 respectively. Fig. 12f shows that 5% (run 8) and 6.95% (run 3) of OPC-LBPA-MK has predicted compressive strength of 19.06 and 17.06 N/mm^2 in Sulphate. At 8.825% (run 2), 10.655% (run 1), and 12.5% (run 10), the estimated strengths are 23.2, 18.58, and 19.06 respectively. At 15.2% (run 11), 17.75% (run 10) and 20% (run 4) the predicted strengths are 25.0, 14.98, and 25.0 N/mm^2 respectively.

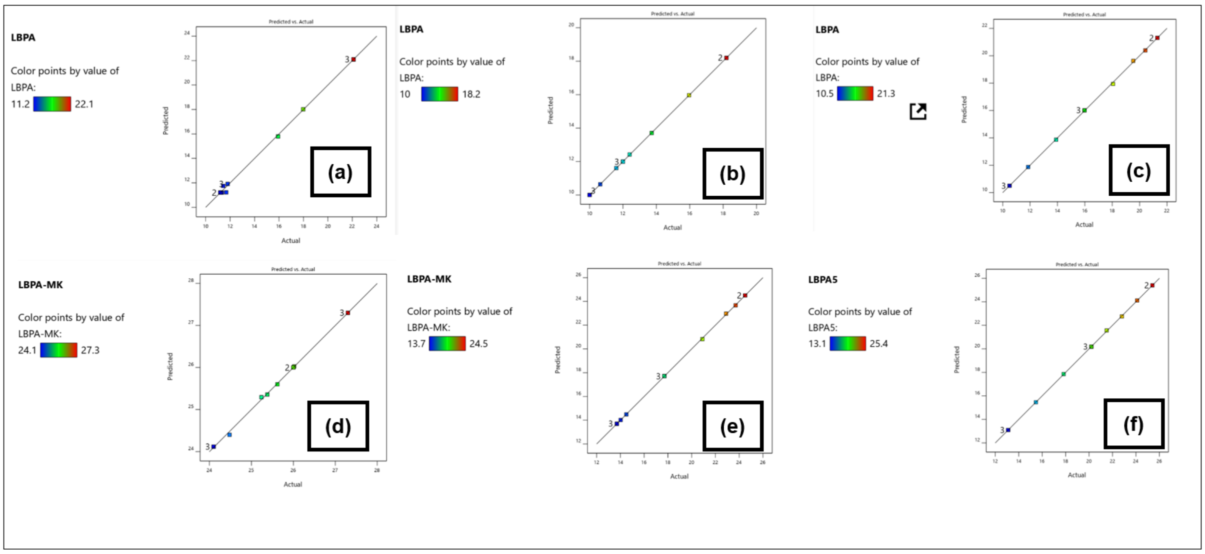

Fig 9. Predicted vs. actual values plot for a. OPC-LBPA: HCl, b. OPC-LBPA: H_2SO_4, c. OPC-LBPA: Sulphate, d. OPC-LBPA-MK: HCl, e. OPC-LBPA-MK: H_2SO_4, f. OPC-LBPA5: Sulphate.

This figure shows line graphs for each of the concrete blend. The lines were in a straight line showing a linear relationship and the proposed model terms were sufficient, and constant variance assumption was verified.

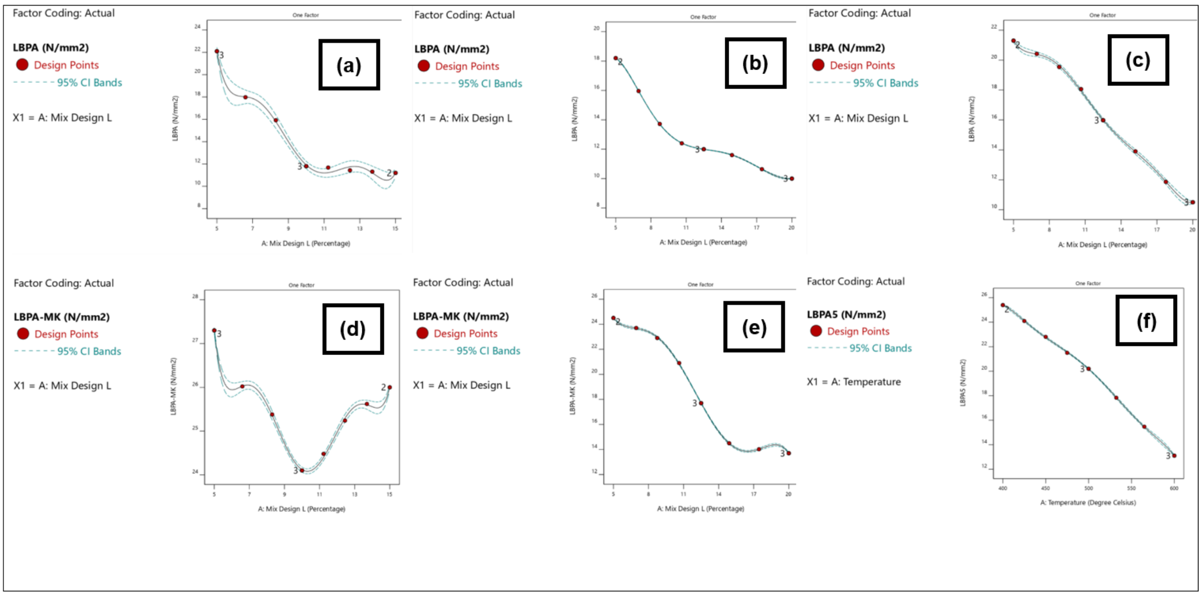

Fig 10. The 2-D plots for a. OPC-LBPA: HCl, b. OPC-LBPA: H_2SO_4, c. OPC-LBPA: Sulphate, d. OPC-LBPA-MK: HCl, e. OPC-LBPA-MK: H_2SO_4, f. OPC-LBPA-MK: Sulphate.
This figure shows biaxial graphs indicating the relationship between LBPA and MK content and mix design.

Table 8 shows validation of the optimized model. In engineering applications generally, a variability of 20% of error percentage is regularly acceptable (Baji, 2014; Manan *et al.*, 2021).

Fourteen of the response variables of compressive strength (extreme pH) observed error percentages within the acceptable ranges. The response variable of strengths observed error percentages within the acceptable ranges for OPC-LBPA: HCl are 0.02% (L05), 0.56% (L0) and 17.80% (L15). The response variables of strengths observed error percentages within the acceptable ranges for OPC-LBPA: H_2SO_4 are 0.04% (L05) and 2.52% (L10). The response variable of strengths observed error percentages within the acceptable ranges for OPC-LBPA: Sulphate are 0.05% (L05) and 0.21 (L10). The response variable of strengths observed error percentages within the acceptable ranges for OPC-LBPA-MK: HCl are 0.02% (L05M15), 1.11%

(L10M15) and 13.10% (L15M15). The response variables of strengths observed error percentages within the acceptable ranges for OPC-LBPA-MK: H_2SO_4 are 0.01% (L05M15), 3.68% (L10M15), 1.93% (L15M15) and 5.86% (L20M15). The remaining were out of ranges. This shows that the optimized prediction model of compressive strength (Eq. (4)) in relation to percentages of LBPA is the most accurate compared to others.

Table 8. Validation of optimized models.

Mix	Mix Design	Compressive Strengths (N/mm^2) under HCl		Percentage Error (%)	Compressive Strengths (N/mm^2) under H_2SO_4		Percentage Error (%)	Compressive Strengths (N/mm^2) under Sulfate		Percentage Error (%)
		Experimental	Predicted		Experimental	Predicted		Experimental	Predicted	
OPC-LBPA	5	22.1	22.10	0.02	18.2	18.19	0.04	21.3	21.31	0.05
	10	11.8	11.73	0.56	12.6	12.28	2.52	19.1	19.14	0.21
	15	11.2	9.21	17.80	11.6	6.56	43.46	13.9	19.81	42.50
	20	10.9	871.22	7,892.84	10	18.17	281.77	10.5	42.59	305.61
OPC-LBPA-MK	5	27.3	27.30	0.02	24.5	24.50	0.01	25.5	304.22	1,093.02
	10	24.1	23.83	1.11	22.5	21.67	3.68	22.7	67.35	196.70
	15	26	22.59	13.10	14.5	14.22	1.93	25	361.02	1,344.08
	20	13.2	392,022.11	2,969,764.47	13.7	12.90	5.86	20.5	1,606.03	7,734.29

IV. CONCLUSION

The study examined fresh and mechanical properties of binary and ternary concrete made with OPC, LBPA and MK. The following conclusions were made from the study:

- Workability (slump and compacting factor) decreased as the LBPA and MK replacement level increased for both binary and ternary systems.
- Setting times increased with increase in LBPA and MK content for binary and ternary blends.
- Mechanical properties (compressive, tensile and flexural strength) improved as the LBPA content increased for the binary concrete. The optimum LBPA replacement was found to be less than 10% with drastic reduction in strength beyond this replacement level.
- For the ternary blend, mechanical properties (compressive, tensile and flexural strength) improved with the inclusion of 15% MK. The maximum strength was obtained at combined 20% LBPA-MK replacement.
- LBPA and MK Water absorption resistance of concrete
- Inclusion of LBPA and MK results to improved resistance to extreme pH and elevated temperature.
- The optimum LBPA and MK replacement was found to be L20M15 (20% LBPA and 15%MK) with notable loss in strength beyond this replacement level.
- The optimized model of OPC-LBPA (L05) and OPC-LBPA-MK (L05M15) had the highest accuracy with percentage errors of 0.2% compared to other parameters.

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Author Contributions

FN Isa: Conceptualization, Methodology, Analysis, Writing – original draft & editing. MAM Johari:

Supervision, review & editing, I Anum: Supervision, review & editing. LJ Agabus: Analysis, review & editing.

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The authors declare no conflict of interest.

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