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Modelling the Chloride Induced Strength Loss Index of Periwinkle and Clam Shell Ash Hybridized Pozzolan in Concrete

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ABSTRACT :*With the aim of sustaining or improving on the durability indices of pozzolans while advancing on their efficiency geared towards the sustainability requirements of reduction in cement production, this study simultaneously examines the mechanical and durability behavior of ternary blended cement made up of Portland limestone cement, calcined periwinkle, and clam shell ashes in concrete subjected to a chlorinated solution. Calcination temperature, synergistic ratio, compressive strength and chloride induced strength loss index, were all enhanced and optimized using combined I-optimal mixture design, which utilized laboratory-analyzed data to statistically develop models for a ternary blended cement concrete cured in a 10% chlorinated medium. At age 28days, a chloride induced strength loss index of 12.72% was recommended for an optimized mixture configuration of 54.6%PLC:25.1%PSA:20.3%CSA at a calcination temperature of 606.7%, which was 51.8% of the strength loss of plain cement concrete of 24.56%. Developed model can be applied in circumnavigating the design space to meet specific structural, local, global, economic and environmental needs.*

KEYWORDS *Calcination Temperature, CISLI, Compressive strength, Pozzolana Concrete, Synergistic Ratio*

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I. INTRODUCTION

Sea water contains high quantities of chlorides and sulfates, marine settings are extremely harsh on concrete structures, reducing their long-term durability and causing significant economic loss [1]. Concrete is one of the most commonly used building materials in today's construction [2]. Cement and other cementitious materials such as fly ash and slag cement, aggregate (usually a coarse aggregate made of gravels or crushed rocks such as limestone or granite, plus a fine aggregate such as sand), water, and chemical admixtures make up this composite construction material [3, 4]. The most common problem impacting the durability of reinforced concrete structures is corrosion of steel reinforcement in concrete and one of the main processes of deterioration impacting the long-term performance of such systems is chloride-induced corrosion [5]. [6] Concrete protects the reinforcing steel from penetrating chlorides, which can cause steel depassivation and raise the danger of corrosion. Chloride resistance is determined by the concrete's permeability and the thickness of the reinforcing cover. The most effective technique to prevent chloride ion penetration is to reduce the water–cement ratio, according to the numerical analysis of the internal and external conditions associated with chloride attack [6, 7]. [6] added that concrete's chloride resistance is strongly dependent on its porosity in terms of pore size, pore distribution, and pore system interconnectivity. The type of cement and other mix ingredients, as well as concrete mix proportions, compaction, and curing, all influence the porosity of concrete. This carefully informs that whilst minimizing water to binder ratio, a primary contribution towards a more chloride resistive concrete could be on increasing the specific gravity of the binder.

Pozzolans are mostly described as siliceous in nature [18 -21] as the reactivity is based on the reaction between silicic acid and calcium hydroxide. However, there is a thin line between pozzolanicity and hydraulicity which is function of the siliceous and calcareous composition of the material [22]

The use of pozzolans in cement structures has been priced for its contribution in enhancing the durability of concrete by reducing concrete's porosity/permeability as well as eating up the aluminate phase and calcium hydroxide components of Portland cement by replacement and pozzolanic activity respectively [8 – 14, 17]. Yet noted for strength reduction at proportions of binder exceeding 15% in concrete and mortar [23 – 27].

Self-cementing capabilities in pozzolans are due to a high concentration of CaO; however, the activity of pozzolans is dependent on an acid-based reaction that requires the presence of SiO_2 [15,16]. Yet the efficiency of cement replacement materials are limited either by availability, oxide composition limitations (lacking in self-cementing potentials required for early strength contribution) or limitations in knowledge for optimized pozzolana production parameters. Whilst it's a timely requirement to invest scientific tools in understudying the possibilities of increasing the replaceability of Portland cement in engineering structures, it is only logical to simultaneously ascertain the durability indices associated with it.

This research therefore aims to establish knowledge on the potentials of synergized agro-based materials calcareously and siliceously complementing in nature and calcined optimally on concrete's chloride related durability indices relative to early strength losses.

II. MATERIALS AND METHODS

Shells of periwinkles and clams were collected from the area surrounding the main market in Amassoma, Bayelsa state. To eliminate organic matter and moisture, samples were washed and sun dried for 48 hours. Following that, samples were broken down with a hammer mill, synergized interchangeably at varying synergistic ratio ranging from (30% - 70%) and samples with a micron size smaller than 600 were prepared for calcination. Calcination was carefully monitored in the absence of oxygen, at a rate of about 10°C per minute, with an extra 30 minutes for homogeneity and finally pulverized to achieve a fineness of more than 50% passing 90micron sieve This study used the typical concrete materials of Portland cement, fine aggregate (sand), coarse aggregate (granite), and water in the production of a grade M20 concrete at a norminal weight batching mix ratio of 1:2:4. Primary and hybrid pozzolanic materials were combined with cement to form a ternary blended binder component.

The investigation's major research materials were categorized as agricultural pozzolans (AP). Clam shell ash (CSA) and Periwinkle shell ash (PSA) are two of them. The hybrid research materials were created through the synergistic production of five (5) sets of hybrid materials with complementary calcium and silicon oxides. Mass proportioning was done in the ratios of 70:30, 60:40, 50:50, 40:60, and 30:70. These were calcined at five (5) different temperatures: 25°C, 200°C, 400°C, 600°C, and 800°C. As a result, a total of 35 hybrid samples were created as part of this study's hybrid research samples and used to partially replace cement in concrete at five different levels: 0%, 20%, 30%, 40%, and 50%. Using a constant water to binder ratio of 0.5, 2 sets of three cubes (150mm*150mm*150mm) where produced per temperature, per replacement level and per synergy, making a total of 852cube specimens (See Table 1 for comprehensive breakdown).

Curing technique was made uniform for concrete samples cured in fresh water as well as those cured in chlorinated solution. 24 hours after production of concrete specimens, both sets of specimens were demolded from their respective molds and inserted into their already prepared curing solutions for a period of 28days. This was done with a logical intent to understudy the effect of chloride attack on pozzolana concrete at its weakest state (pre-hydration state). The difference between the strength's obtained from both media divided by the strength of the fresh water media and taking to a percentage is recorded as the chloride induced strength loss index (CISLI). Test methods for particle size distribution, binder/pozzolan fineness, specific gravity, slump, compressive strength and CISLI are in accordance to standard methods referenced in Table 1.

Table 1: Tests Methods

S/N	Test Method	Test standard	Synergy A	Replc. Level B	Temp.Level C	Spec. per age E	Control spec. F	Total Spec. (A*B*C*E) +F
1	Particle Size Distribution for Fine Aggregate	[28]	-	-	-	-	-	-
2	Particle Size Distribution for Coarse Aggregate	[28]	-	-	-	-	-	-
3	Fineness Test*	[29], [30]	7	-	5	-	1	36
4	Specific Gravity	[31]	7	-	5	-	1	36
5	Water Demand/Slump/ Workability	[32]	-	-	-	-	-	-
6	Compressive Strength	[33]	7	4	5	3	9	429
7	CISLI	[1], [3]	7	4	5	3	9	429

III. RESULTS AND DISCUSSIONS

The gradation results obtained showed a zone 3 fine aggregate and a well graded coarse aggregate. Fineness was greatly enhanced by calcination temperature with a direct linearized relationship. Calcination temperature was observed to have a quadratic effect on the specific gravity of the pozzolans with synergistic ratio having a limited effect. Increasing calcination temperature as well as increasing CSA content increased the slump and reduced the water demand of the PSA/CSA pozzolana concrete. Table 2 represents the 28day compressive strength of the PSA/CSA pozzolana concrete cured in both clean water as well as a chlorinated medium for a period of 28days post hydration phase. Developed models from table 2 were used to study the effect of synergistic ratio, calcination temperature, and pozzolanic concentration on the chloride resistivity of PSA/CSA pozzolana concrete.

Table 2: 28day concrete compressive strength results for clean water and chlorinated water curing media

H20 CURING MEDIUM						CHLORINATED CURING MEDIUM				
20% cement Replacement Level										
Temperature	**25ºC**	**200 ºC**	**400 ºC**	**600 ºC**	**800 ºC**	**25ºC**	**200 ºC**	**400 ºC**	**600 ºC**	**800 ºC**
CONTROL	27.74					20.93				
100P	18.77	19.22	20.28	21.55	22.95	15.18	17.45	20.01	19.58	15.60
70P	19.56	20.39	21.68	22.87	23.40	13.85	17.74	21.38	17.61	16.87
60P	21.66	23.75	24.67	25.67	27.04	13.98	20.30	22.44	19.83	18.52
50P	23.28	23.70	24.11	24.72	25.54	12.00	19.23	20.63	18.94	17.89
40P	20.71	21.08	22.09	23.31	23.85	11.40	19.25	19.84	18.22	17.37
30P	20.25	21.07	22.04	23.67	24.11	12.91	17.60	19.08	16.31	18.21
100C	18.28	19.15	20.31	22.28	23.22	13.05	18.94	19.71	19.97	19.23
30% cement Replacement Level										
100P	17.55	17.73	18.09	19.58	22.55	14.78	17.18	19.55	15.74	14.85
70P	18.49	20.38	20.47	21.56	22.03	12.26	18.37	20.61	17.77	12.38
60P	22.12	22.40	23.75	24.67	25.42	11.00	18.62	21.19	19.07	11.24
50P	19.74	22.50	22.34	22.77	24.44	13.06	20.77	20.17	19.52	13.06
40P	18.23	18.88	19.26	20.90	23.05	11.90	20.63	19.23	18.19	17.45
30P	18.08	19.11	19.50	20.37	21.64	12.28	17.61	19.24	18.61	16.71
100C	17.33	18.55	19.19	19.83	20.45	11.88	18.64	19.09	18.48	16.74
40% cement Replacement Level										
100P	16.78	17.02	17.44	18.27	18.87	14.80	16.44	16.45	14.74	14.61
70P	17.47	18.87	20.17	20.81	21.11	16.72	17.17	17.43	19.39	15.02
60P	19.96	20.10	21.22	21.67	23.71	16.97	17.77	18.22	20.35	17.02
50P	17.13	18.88	19.28	19.13	19.78	16.78	17.17	17.33	20.03	16.73
40P	16.54	17.22	17.84	17.77	20.53	14.37	15.55	16.18	20.01	17.14
30P	16.28	16.92	18.15	19.40	21.19	14.83	15.33	16.87	19.11	18.47
100C	16.12	16.81	18.73	19.21	19.62	12.04	16.43	17.27	19.13	16.31
50% cement Replacement Level										
100P	15.04	15.25	16.13	17.74	17.86	10.76	11.26	12.32	14.26	14.00
70P	15.17	16.52	17.25	18.27	18.55	11.22	13.17	13.67	14.75	15.59
60P	17.20	18.02	18.60	19.21	19.73	12.92	14.78	15.11	17.16	16.12
50P	16.41	16.70	17.33	17.55	18.09	13.46	13.82	14.54	16.71	14.63
40P	16.33	16.88	17.09	17.08	18.18	13.03	12.41	13.01	17.02	12.04
30P	15.30	17.11	17.21	17.78	18.26	12.42	11.63	13.01	17.05	15.44
100C	14.80	15.32	15.51	15.66	16.58	11.22	13.18	14.17	15.35	14.64

Table 2 represents the effect of cement level replaced, calcination temperature as well as pozzolan synergistic ratio on the compressive strength of plain and pozzolana concrete cured in fresh water as well as 10% chlorinated media. Surface results for compressive strength of concrete cured in fresh water indicate a reduction in strength relative to increase in cement replacement level, increase in strength relative to increase in calcination temperature, and a hugging quadratic relationship relative to synergistic ratio and cresting around 60PSA:40CSA synergistic configuration.

Table 3 ANOVA and Coefficient of Regression for chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

Mixture Components **A B C**

Process Factors **D**

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	1831.64	8	228.96	7.65	0.0001	significant
[1]Linear Mixture	21.37	2	10.69	0.36	0.7043	
AB	814.51	1	814.51	27.22	< 0.0001	
AC	135.38	1	135.38	4.52	0.0467	
CD	107.75	1	107.75	3.60	0.0730	
CD^2	89.11	1	89.11	2.98	0.1006	
ABD^2	291.19	1	291.19	9.73	0.0056	
ACD^2	232.53	1	232.53	7.77	0.0117	
Residual	568.48	19	29.92			
Cor Total	2400.13	27				

Coefficient of Regression

Std. Dev.	5.47	R-Squared	0.7631
Mean	15.46	Adj R-Squared	0.6634
C.V. %	35.38	Pred R-Squared	0.5397

CISLI Model: Model for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

CISLI =
+0.24074 * PLC
+0.23837 * PSA
-0.51456 * CSA
-1.70490E-004 * PLC * PSA
+0.014906 * PLC * CSA
+8.19494E-003 * PSA * Calc. Temp
+6.30122E-003 * CSA * Calc. Temp
-1.63899E-004 * PLC * PSA * Calc. Temp
-1.52968E-004 * PLC * CSA * Calc. Temp
-9.93326E-006 * PSA * Calc. Temp^2
-7.97410E-006 * CSA * Calc. Temp^2
+1.98665E-007 * PLC * PSA * Calc. Temp^2
+1.85416E-007 * PLC * CSA * Calc. Temp^2

Table 3 represents the analysis of variance and coefficient of regression for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete. The developed model is a combination of a quadratic mixture component and quadratic factor type model, having seven model classes of linear mixture, AB, AC, CD, CD^2, ABD^2 and ACD^2, which are all integrated into a significant model having a $P<<0.05$ and negating the null hypothesis.

The ratio of the model to total sum of squares gave a coefficient of regression of 0.7631. accordingly, adjusted and predicted coefficients of regression was obtained as 0.6634, 0.5397, indicating a statistically sound model prediction capacity.

Standard deviation was 5.47 about a mean 15.56, yielding an error coefficient of 35.38% (C.V). The adequate precision of the model was obtained as 8.56, indicating that a single error could be expected for every 8.56 predictions. This is greater than the minimum allowable associated error of 4, hence the model indicates an adequate signal and can be used to circumnavigate the design space.

Model diagnostics as shown in Fig. 1 represents a relative distribution of the externally studentized errors. The model can hence be adopted as statistically satisfactory.

Model coefficients obtained for the model represented the absence of multicollinearity effect for all the model components as no variance inflated factor was seen to be greater than 10. This implies a statistical flexibility between independent variables and a good requirement for testing the effect of varying isolated factors on the response variable.

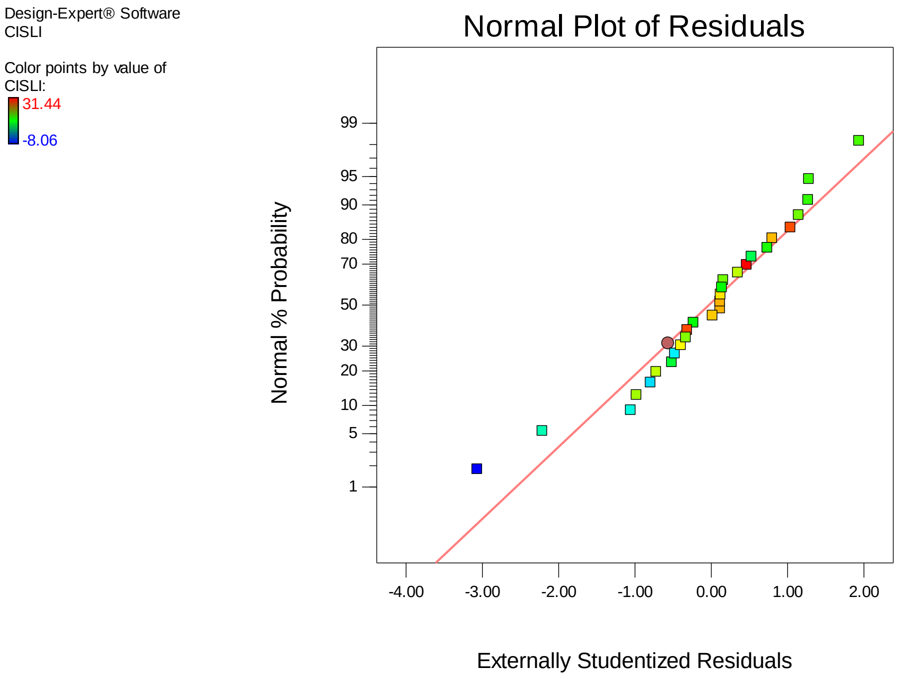

Fig. 1 Plot of externally studentized residual distribution for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

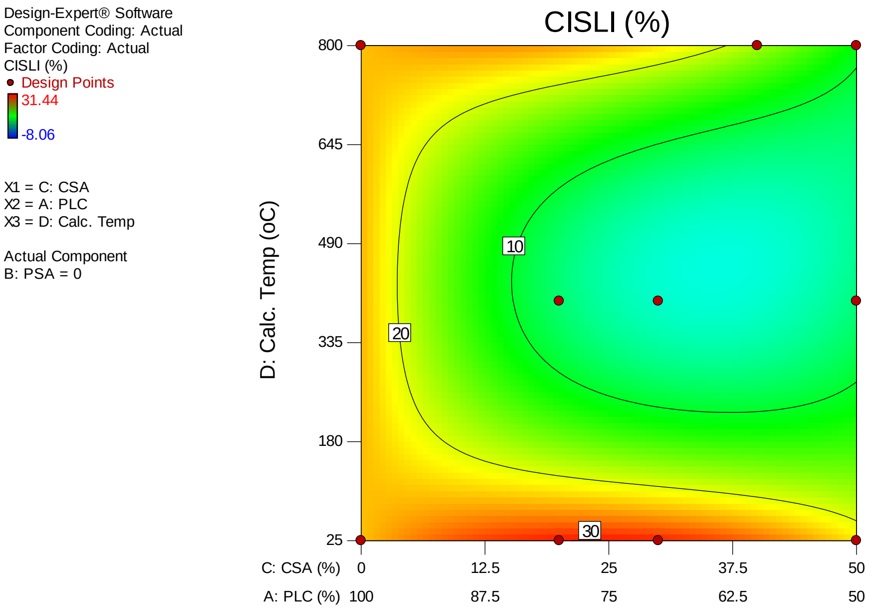

Fig. 2 Plot of model interaction at 0%PSA concentration on the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

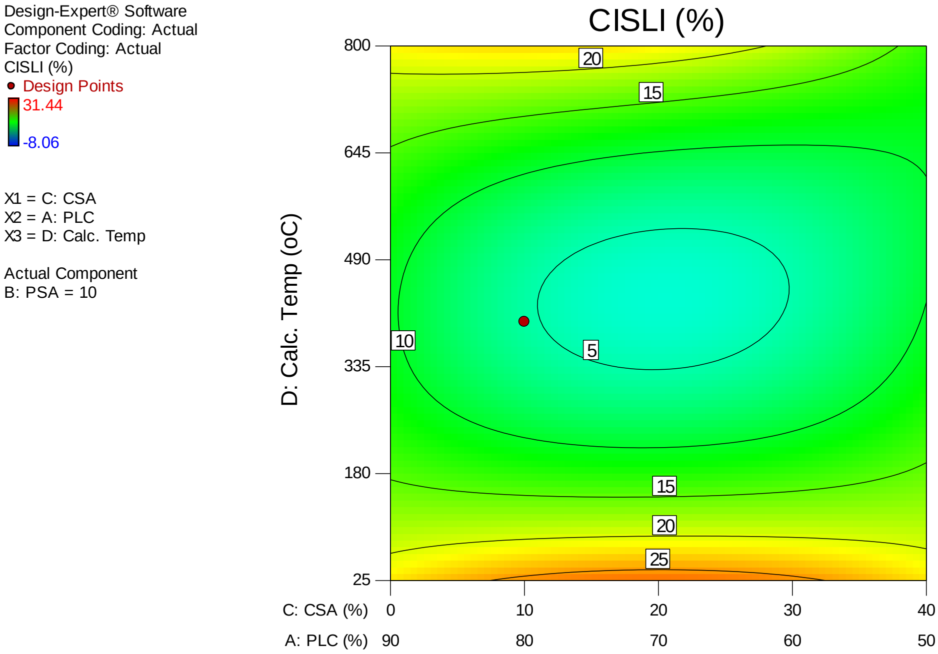

Fig. 3 Plot of model interaction at 10%PSA concentration on the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

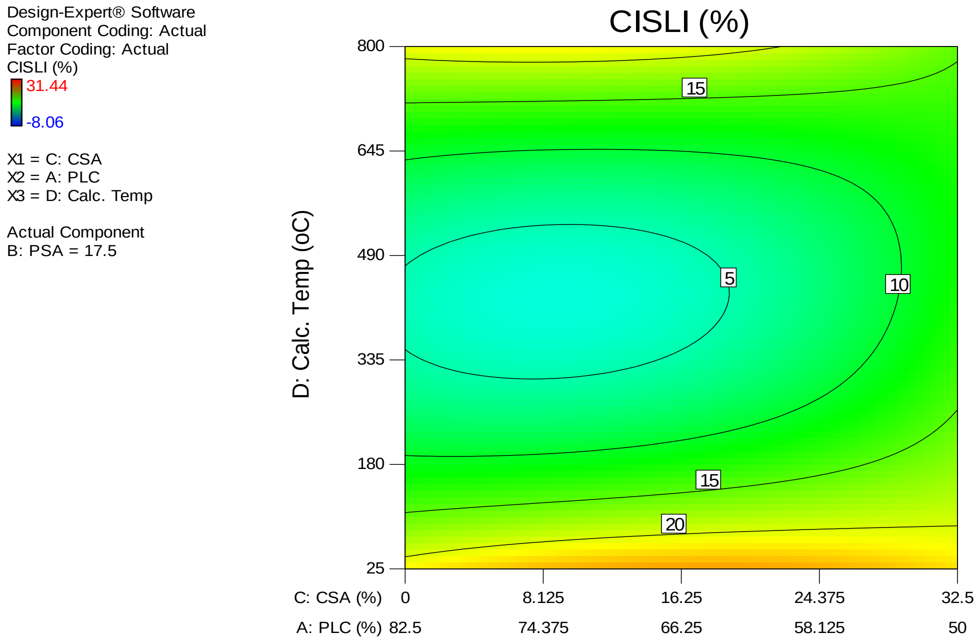

Fig. 4 Plot of model interaction at 17.5%PSA concentration for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

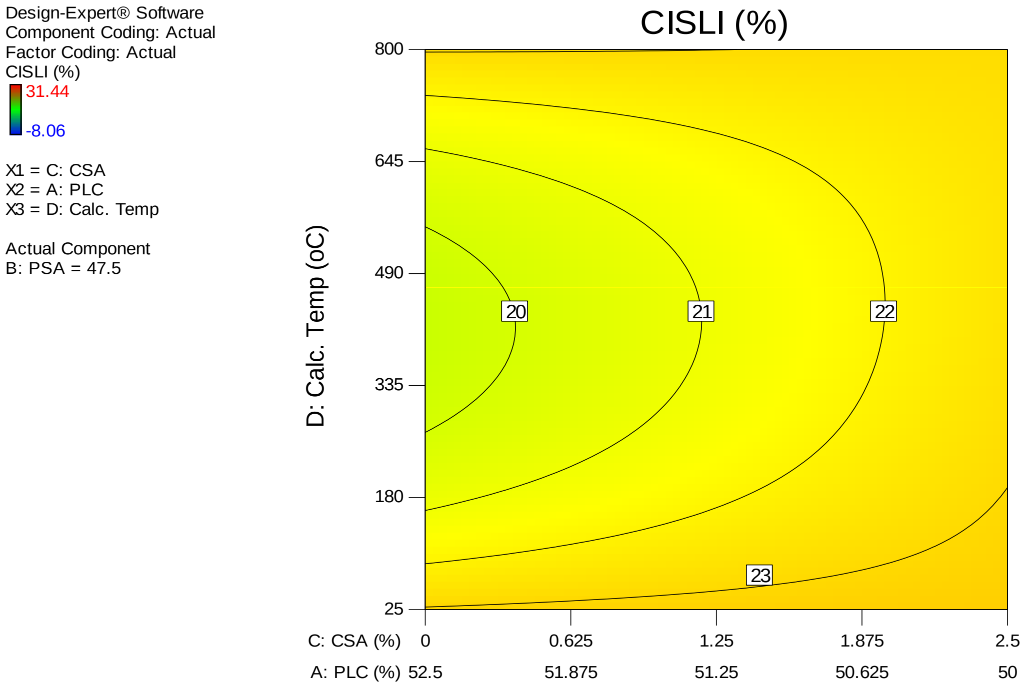

Fig. 5 Plot of model interaction 47.5%PSA concentration for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

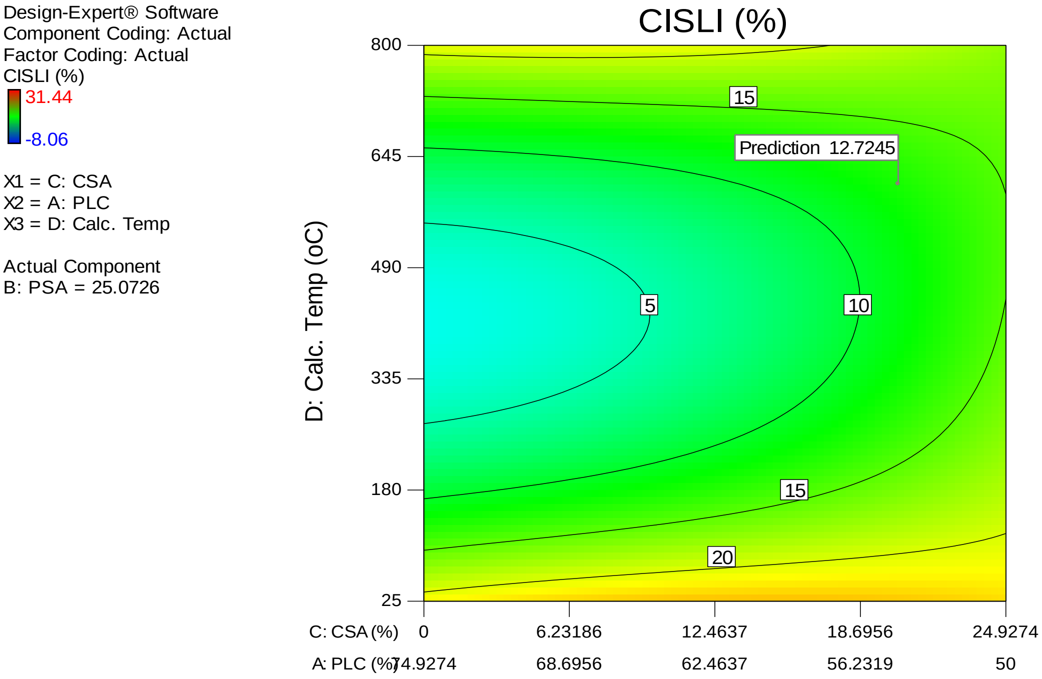

Fig. 6 Plot of optimised model interaction for the chloride induced strength loss index of PSA/CSA hybrid pozzolana concrete

Fig2. – Fig 5. are extracts from the model interaction between the mixture and process components of the model. The effect of the process factor (calcination temperature) on the CISLI of the PSA/CSA hybrid pozzolana concrete was observed to be quadratic, sagging with a trough ranging between 180^{o}C and 645^{o}C for all mixture configurations. Fig. 2 – 5, represents the effect of varying periwinkle shell content on the CISLI of PSA/CSA pozzolana concrete. At 0%PSA content, the quadratic PLC: CSA mixture had a CISLI trough range between 25% - 50%CSA content. Increasing PSA concentration to 10% leads to a shift in the CISLI quadratic trough range to between 10% and 30% CSA. Similarly, at 17.5% PSA concentration, a further decline in CISLI trough range was observed between 0 and 16.25%. This is a clear indication that to maintain minimal compressive strength losses in PSA/CSA hybrid pozzolana concrete due to chloride induced attack, there is a need to reduce the CSA concentration for every increase in PSA content.

At optimization (Fig. 6), synergizing the custom constraint at a mixture configuration of 54.6%PLC:25.1%PSA:20.3%CSA at a calcination temperature of 606.7% yielded a CISLI of 12.72% and observed to be 51.8% of the control of 24.56%. Hence, the application of these findings in the construction sector is feasible and mostly for non-reinforced to lightly reinforced structures such as plain concrete structures.

IV. CONCLUSION

Having experimentally and statistically observed the combined effect of calcination temperature, synergistic ratio as well as pozzolana concentration on the chloride resistivity of PSA/CSA blended cement concrete, the following conclusions can be drawn;

- Calcination temperature when optimized, enhances pozzolana concrete's strength and durability
- The need for synergy in pozzolana production is quite essential in order to develop a self-cementing pozzolana
- Optimized calcination temperature and pozzolana synergy, enhances pozzolana concentration in pozzolana concrete
- Using periwinkle shell and clam shell ash as a case study, responses of strength and durability are better enhanced with increasing PSA content against CSA content.
- Optimum temperature for the calcination of PSA/CSA pozzolan ranges between 350^{o}C and 650^{o}C
- Cement replaceability using PSA/CSA pozzolana can be greatly improved to levels beyond 50% by mass at a more controlled fineness, yielding acceptable strength and durability results.

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