EFFECTS OF SILICA FUME AND METAKAOLIN ON PERMEABILITY OF CONCRETE

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ABSTRACT

White portland cement is commonly used in architectural precast concrete when genuine white concrete is desired or as base cement when colors are desired. For such applications metakaolin provides a distinct advantage over silica fume. Supplementary cementitious materials, such as silica fume and metakaolin are often used to improve strength and reduce permeability of concrete. In this investigation, a comprehensive experimental program was developed to assess the permeability of concrete samples in which white portland cement was partially replaced, up to 25% by weight, with pozzolanic admixtures such as silica fume and metakaolin. Water-to-cementitious material ratio was kept constant at 0.45, and comparable workability was achieved through the use of a high-range water-reducing admixture. Rapid chloride permeability tests were performed at different ages according to ASTM C 1202 to include the effect of aging. In addition, select concrete mixtures, containing 10% metakaolin with different water-to-cementitious material ratios were subjected to rapid chloride permeability tests to study the effect of water-to-cementitious materials ratio on concrete permeability. A comprehensive experimental design with sufficient data points and statistical tools used in this investigation helped in the development of accurate models to predict the effect of individual responses on the permeability of concrete.

Keywords: Concrete, Metakaolin, Permeability, Regression analysis, Silica fume, White Portland cement.

INTRODUCTION

Permeability of concrete plays an important role on the durability of concrete, not only the rate of entry of moisture that may contain aggressive chemicals, but also movement of water during freezing and thawing. The single parameter that has significant effect on permeability of concrete is water-to-cement ratio (w/c).[1] A decrease in w/c ratio results in reduced porosity in cement paste and, hence, the concrete becomes more impermeable. Also, the microstructure of the transition zone between the aggregate and the cement paste may affect the strength of concrete and its permeability. While water-to-cement ratio has significant influence on strength and permeability of concrete, one can further achieve impermeability through the addition of supplementary cementitious materials. Another factor that significantly influences permeability of concrete is aging due to densification of matrix. Thus, permeability of concrete is a function of the permeability of cement paste, aging, aggregate, and aggregate-cement paste interface (transition zone).[1 - 4]

Supplementary cementitious materials, such as metakaolin and silica fume, have been observed to reduce the permeability of concrete significantly.[1-8] Silica fume consists primarily of amorphous (non-crystalline) silicon dioxide (SiO_2). Metakaolin ($2SiO_2$, Al_2O_3), a calcined china clay, is a largely amorphous dehydration product of Kaolinite. The average particle size of metakaolin is 1.3 microns (0.05×10^{-6} in.), which is higher than 0.1 microns (0.004×10^{-6} in.), that for silica fume. While both silica fume and metakaolin are expected to reduce permeability of concrete, their performances differ due to their chemical composition and particle size. Rapid chloride permeability test (ASTM C 1202), used in this research, is an indirect measure of permeability of concrete and the results have been observed to correlate well with water permeability.[9]

RESEARCH SIGNIFICANCE

White portland cement is commonly used for architectural use when genuine white concrete is desired or as base cement when colors are desired. While grey portland cement modified with silica fume and reduced water content has been observed to be highly resistant to penetration by chloride ions, to the best of author’s knowledge, no systematic study has been performed on white portland cement concrete modified with silica fume or metakaolin. In this comprehensive experimental investigation, key factors that influence permeability of concrete were identified through factorial design. Multiple regression models were then developed to predict permeability of concrete as a function of these key factors.

EXPERIMENTAL PROGRAM

MATERIALS AND MIXTURE PROPORTIONS

The cementitious materials used in this investigation were white portland cement, silica fume, and metakaolin. White portland cement is commonly used in architectural precast panels when light color is desired. Metakaolin is well suited for such applications. However, the properties of white and non-white Portland cement are same and as such the performance of concrete are similar. Fine aggregates (fineness modulus of 2.95), coarse aggregates (maximum nominal size of 6.25 mm, 0.25 in.), water, and superplasticizer, along with cementitious binder, were properly proportioned to achieve the objectives of this research. Table 1 presents the details of mix ingredients and their proportions. White portland cement matrix was partially replaced, up to 25 % by weight, with pozzolanic admixtures, such as silica fume or metakaolin. Water-to-cementitious material ratio was maintained at 0.45, and comparable workability was achieved through the use of superplasticizer. It should be noted that the water demand for both silica fume and metakaolin are comparable. It is reasonable to assume that the effect of water remains the same in both matrices. Thus, water-to-cementitious material ratio was not a parameter in our statistical analysis to arrive at regression model. Mixing was done in accordance with ASTM C 192.

Typically for bridges, 10-15% replacement of cement with silica fume is specified. However, higher dosages were included in this investigation to generate sufficient data points to perform a robust statistical analysis. The 20 and 25% dosages of metakaolin and silica fume used are unrealistically high and are not economical. However, metakaolin has been used to improve durability of glass fiber reinforced cement composites in the range of 20 – 25% replacement of cement.[10]

Table 1 – Test Series and Mixture Proportions

Mix	Type of Cement	Superplasticizer-to-Cementitious Material ratio	Metakaolin, %	Silica Fume, %
1	Grey	0.005	0	0
2	White	0.005	0	0
3	White	0.0075	5	0
4	White	0.0075	0	5
5	White	0.01	10	0
6	White	0.01	0	10
7	White	0.0125	15	0
8	White	0.0125	0	15
9	White	0.015	20	0
10	White	0.015	0	20
11	White	0.0175	25	0
12	White	0.0175	0	25
13	White	0.005	10	0
14	White	0.015	10	0

CURING AND SAMPLE PREPARATION

From each concrete mixture, cylinders of 101.6 mm (4 in.) diameter and 203.2 mm (8 in.) height were cast. All the specimens were covered with plastic lids for 24 hours. They were then demolded and immersed in water for 7 days, the age of first samples subjected to permeability test. Three specimens of 101.6 mm (4 in.) diameter and 50.8 mm (2 in.) thick were cut from each cylinder using a diamond saw, for rapid chloride permeability testing. Minimum of 9 specimens were tested for any given age and mixture proportion to better analyze chloride permeability of concrete using statistical tools.

RAPID CHLORIDE PERMEABILITY TEST (RCPT)

The principle of Rapid Chloride Permeability Test procedure (ASTM C 1202) is to measure the amount of electrical current passed through the concrete sample exposed to the potential of an electric field over a fixed period of time. The test involves application of 60 V dc between the ends of the specimen with solutions of sodium hydroxide and sodium chloride on opposite sides. The total charge passed (Coulombs), according to ASTM C 1202, is a measure of electrical conductance and is used to evaluate the permeability of concrete. Results obtained from RCPT correlate well with the results from conventional methods. However, RCPT measures electrical conductance, and, as such, the results should be analyzed carefully, specifically for concrete with low permeability. It has been reported that low permeability concrete with silica fume tends to exhibit lower charges, compared to similar concrete without silica fume.[1] Similar behavior is expected of concrete with metakaolin. Thus, the results of this investigation could be effectively used to compare the performance of these two low permeability concretes.

TWO-FACTOR FACTORIAL DESIGN

Two-factor factorial design is one of the statistical tools available not only to determine if two factors, A and B, have an influence on the responses, but also to determine if there is a significant interaction between the two factors.[11]

In order to determine which factors are important to take into account in the multiple regression models, a two-factor factorial design was used not only to implement analysis of variance (ANOVA) tables for metakaolin and silica fume responses, but also to obtain empirical models to predict metakaolin and silica fume responses. Each of these empirical models was expressed in function of two independent variables, percentage in admixture, X_1, and age of concrete, X_2. Percent replacement of cement with metakaolin or silica fume was varied from 0 – 25% at regular intervals of 5%. Age of the specimen selected for testing were 7, 28 and 60 days. From the fitted model curves, an attempt was made to obtain the minimum response. Then, Tukey’s method of multiple comparisons was performed between the minimum means of plain concrete and of concrete modified with metakaolin or silica fume. In order to obtain statistically significant results, nine replicated specimens were tested for any given aging and mixture proportion. All the data points were included in the statistical analysis, except the ones in which testing was incomplete. Additional rapid chloride permeability tests were performed on metakaolin and silica fume concrete samples in order to validate the empirical models developed in this investigation.

EXPERIMENTAL RESULTS AND STATISTICAL DATA ANALYSIS

Table 2 presents the charges passed through plain concrete (reference) at 7, 28 and 60 days. Tables 3 and 4 present the charges passed through concrete in which cement was partially replaced with metakaolin or silica fume. From these results it is evident that matrix modification and aging have significant influence on permeability of concrete.

Both metakaolin and silica fume significantly reduce the permeability of concrete. All concretes, when compared at the same age, showed reduction in charges passed with increase in either metakaolin or silica fume content. From these graphs, it is also clear that regardless of the type of concrete, either plain or modified with silica fume or metakaolin, there is a decrease in charge passed when aging is a factor. In other words, concrete becomes progressively and significantly less permeable with time.

Table 2 - Summary of Charges Passed (in Coulombs) for Plain Concrete

Age at Testing, Days	Charges Passed in Coulombs	
	Mean	Standard Deviation
7	3947.18	298.08
28	2888.82	228.99
60	2882.00	231.85

Table 3 - Summary of Charges Passed (in Coulombs) for Concrete Modified with Metakaolin

Metakaolin, %	Charges Passed in Coulombs, Mean (Standard Deviation)					
	7 Days		28 Days		60 Days	
0	3947.18	(298.08)	2888.82	(228.99)	2882.00	(231.85)
5	1111.64	(152.96)	1104.89	(118.00)	840.56	(119.15)
10	696.08	(102.72)	309.42	(107.57)	388.64	(36.32)
15	522.42	(18.83)	149.83	(31.09)	235.64	(18.88)
20	543.17	(128.45)	153.83	(25.02)	104.73	(17.07)
25	713.91	(135.31)	192.82	(15.68)	66.92	(17.25)

Table 4 - Summary of Charges Passed (in Coulombs) for Concrete Modified with Silica Fume

Silica Fume, %	Charges Passed in Coulombs, Mean (Standard Deviation)					
	7 Days		28 Days		60 Days	
0	3947.18	(298.08)	2888.82	(228.99)	2882.00	(231.85)
5	2701.44	(1075.5)	1079.36	(287.58)	1230.44	(54.84)
10	1832.73	(289.67)	780.00	(242.08)	467.08	(75.13)
15	1317.78	(247.09)	162.75	(40.13)	434.08	(59.33)
20	878.67	(234.84)	325.83	(43.54)	184.50	(51.27)
25	652.50	(143.28)	250.73	(50.85)	182.17	(42.65)

LINEAR REGRESSION MODEL

Permeability, measured as charges passed in Coulombs, is presented in Tables 3 and 4, respectively, for concrete modified with metakaolin and silica fume. These data generated were used to perform the analysis of variance for the two-factor factorial design. Based on that result, a second order linear regression model was developed to describe permeability (charges passed) as a function of age, the percentage of admixture and their interaction. The model that best fit the data is a linear regression quadratic model.

$$Y = a + bX_1 + cX_2 + dX_1X_2 + eX_1^2 + fX_2^2 \tag{1}$$

where: Y is a measure of permeability (charges passed in Coulombs),
X_1 is percentage of admixture (metakaolin or silica fume), and
X_2 is age in days

The coefficient of multiple determination (R^2) for the fitted model was 0.8820 for concrete with metakaolin. For concrete modified with silica fume, the coefficient of multiple determination (R^2) obtained was 0.7805. The coefficient of multiple regression is defined as the proportion of variation in the criterion variable that is accounted for by the co-variations in the predictor (independent) variable. The relatively low R^2 value obtained especially from silica fume response could be explained by the fact that some of the factors, not considered in this study, may have some influence. One example may be the changes in particle size distribution. The best fitted models are presented in equations 3, and 4 as well as in graphical forms in Figures 1, and 2, respectively for metakaolin and silica fume concrete.

$$Y = 1859.6 - 133.71X_1 - 21.525X_2 - 0.39689X_1X_2 + 3.8426X_1^2 + 0.30018X_2^2 \tag{2}$$
(for metakaolin)

$$Y = 4131.7 - 211.95X_1 - 90.217X_2 - 1.0347X_1X_2 + 3.7960X_1^2 + 0.82767X_2^2 \tag{3}$$
(for silica fume)

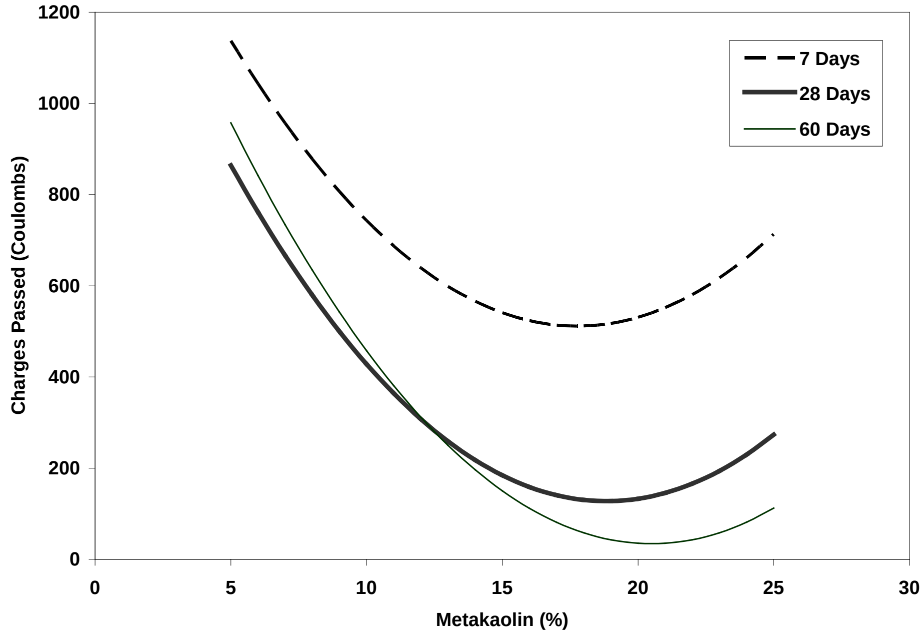

Fig. 1 Second Order Linear Regression Graph for Concrete Modified with Metakaolin

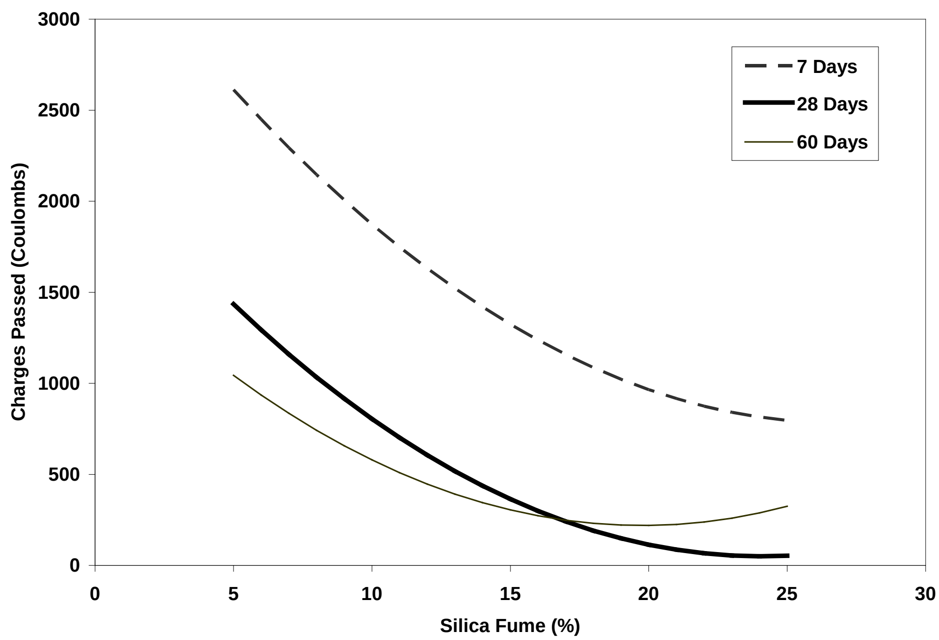

Fig. 2 Second Order Linear Regression Graph for Concrete Modified with Silica Fume

VALIDATION TEST

In order to validate these empirical models developed in this investigation, additional tests were performed on white portland cement concrete modified with metakaolin or silica fume at all percent replacement of cement and age (Tables 5 and 6). Minimum of three specimens were tested at any given percentage replacement of cement and aging condition. Using this additional data, graphs showing predicted charges passed (in Coulombs) versus observed charges passed (in Coulombs) were plotted and are presented in Figures 3 and 4. The empirical models developed were used to obtain the predicted response at any percent replacement of cement and age. From these graphs, we can clearly conclude that the difference between data obtained from the proposed model and experimental observation is insignificant. Thus, the linear regression models developed may be used for accurate prediction of permeability of concrete modified with metakaolin and silica fume (charges passed in Coulombs). The model developed is valid for concrete with percentages of metakaolin or silica fume (X_1) up to 25%, and at any age of concrete (X_2) up to 60 days. The model presented is valid for the water-to-binder ratio and the aggregate proportion used in this investigation. Since the water-to-binder ratio was kept constant and comparable workability was achieved through the use of superplasticizer, the model developed adequately represents the effect of metakaolin and silica fume on permeability. It should be noted that small variation in test results are common when performing tests with concrete. Additional test data are required to refine this model to include the effect of water-to-binder ratio, as well as cement replacement with metakaolin and silica fume on permeability.

Table 5 – Additional rapid chloride permeability test results (charges passed in Coulombs) for concrete modified with metakaolin

Age (No. of Days)	Percentage of Metakaolin				
	5%	10%	15%	20%	25%
7	1205	722	514	342	758
	1028	698	514	420	475
	1141	656	525	383	705
28	906	304	101	140	191
	1126	303	147	135	181
	1159	194	154	120	180
60	856	345	210	95	56
	713	448	215	90	66
	668	408	260	88	50

Table 6 – Additional Rapid Chloride Permeability Test Results (charges passed in Coulombs) for Concrete Modified with Silica Fume

Age (No. of Days)	Percentage of Silica Fume				
	5%	10%	15%	20%	25%
7	2349	2032	1091	934	439
	2201	1993	1394	588	630
	2582	1191	1276	915	641
28	446	730	121	285	136
	1105	764	134	298	266
	846	652	116	244	302
60	1240	519	383	133	130
	1271	405	397	133	157
	1254	459	366	133	200

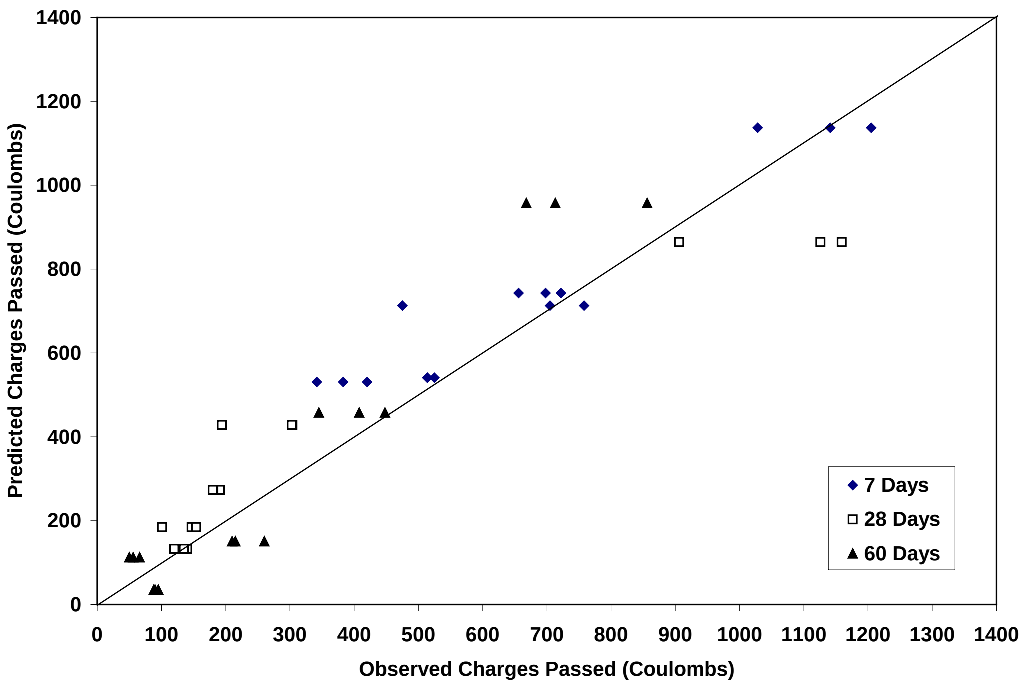

Fig. 6 Comparison of Observed and Predicted Responses for Concrete Modified with Metakaolin

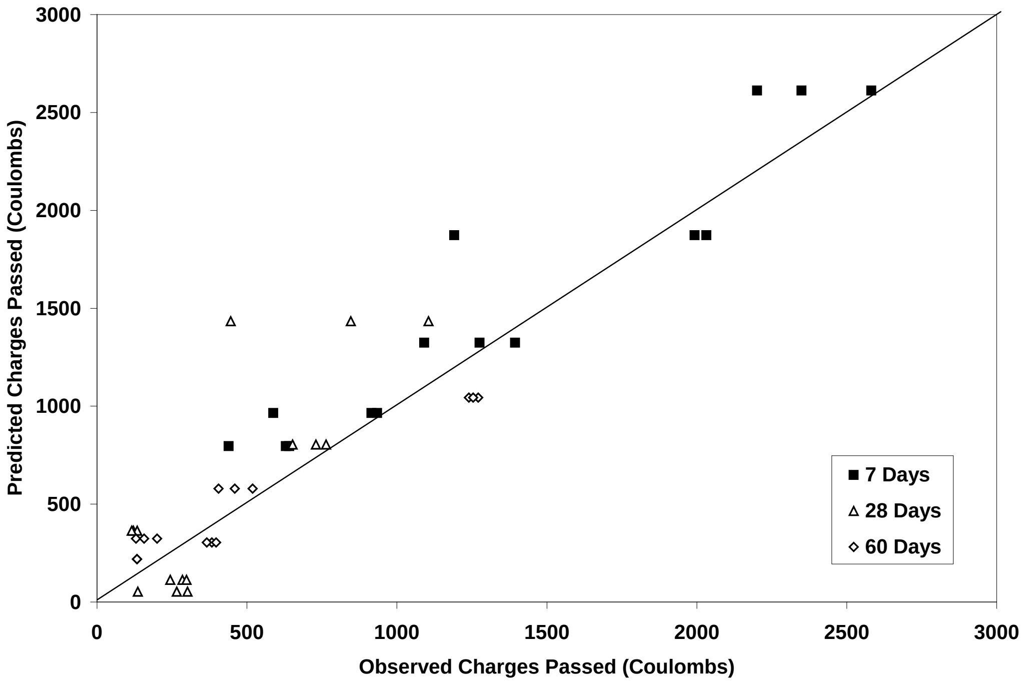

Fig. 7 Comparison of Observed and Predicted Responses for Concrete Modified with Silica Fume

TUKEY'S MULTIPLE COMPARISONS

Several standard methods are available for making paired comparisons of a set of means. One of them, called Tukey's procedure, allows formations of simultaneous 100(1 - α)% confidence intervals for all paired comparisons. Tukey's method compares all possible pairwise differences of means at the same time. The method is based on the studentized range distribution.[10] In the case of this investigation, Tukey's multiple comparisons were made between minimum means of charges passed at specific age and replacement of cement at 95% confidence intervals. The data used for this analysis included additional tests performed for validation of linear regression model developed.

It is clear from Figures 1 and 2, that the minimum charges passed were obtained at 60 days and 20% replacement of cement with metakaolin or silica fume. Tukey's method of multiple comparisons was then performed between the means of plain concrete and metakaolin, plain concrete and silica fume, and metakaolin and silica fume at 60 days (at 20% of metakaolin or silica fume). All factors used during the comparisons were computed and are presented in Table 7. From the matched- pairs designs, the authors arrived at the following conclusions:

- $P(2605.05 \leq \mu_1 - \mu_2 \leq 2949.50) = 95\%$, which leads to the conclusion that metakaolin reduces the penetration of chloride ingress in concrete.

- $P(-113.37 \leq \mu_2 - \mu_3 \leq -46.17) = 95\%$, which leads to the conclusion that metakaolin is more efficient than silica fume in reducing the chloride ingress in concrete.

Where μ_1 represents the population mean for plain concrete, μ_2 for concrete with metakaolin and μ_3 for concrete with silica fume.

Table 7 – Factors involved in Tukey's multiple comparisons

Matrix	Number of Observations	Population Mean at 60 Days	Population Standard Deviation	Tukey's Coefficient $T = (1/2)xq_{(0.05, 3, 28)}$
Plain concrete	8	$\mu_1 = 2882$	216.88	2.2415
Metakaolin Concrete	11	$\mu_2 = 104.7$	16.243	2.2415
Silica fume Concrete	12	$\mu_3 = 184.5$	49.084	2.2415

This statistical analysis substantiates our earlier conclusion that, while both metakaolin and silica fume reduce chloride permeability of concrete, metakaolin performs significantly better. Optimum dosage of metakaolin or silica fume to reduce permeability is 15 – 20%. Higher dosage may even be harmful, due to difficulty in achieving proper workability. With increased dosage, permeability stabilizes, and there is no significant change. For metakaolin concrete, the regression curves rise even when the dosage is increased beyond 20% (Figure 1). This observation was quite evident during early age testing (7 and 28 days). However, with increased aging, it was not obvious. It should be noted that all data points were included in the statistical analysis for developing the regression model.

SUMMARY AND CONCLUSIONS

Based on the data recorded and analysis performed in this investigation, the following general conclusions may be drawn:

- The use of admixture in the concrete, such as metakaolin and silica fume, reduces the permeability of concrete.
- The permeability of concrete reduces with increase in silica fume or metakaolin replacement.
- Concrete becomes progressively less permeable with time. This phenomenon is observed for all types of concrete investigated in this research.
- Metakaolin replacement is more effective than silica fume in making the concrete less permeable. Also, Tukey's multiple comparison performed confirms this deduction $P(-113.37 \leq \mu_2 - \mu_3 \leq -46.17) = 95\%$. Where, μ_2 and μ_3 are population means of charges passed at 60 days, for concrete modified with 20% of metakaolin or silica fume, respectively.

- The statistical regression analysis performed substantiates the experimental observations of this research. Suitable empirical models were developed and validated with additional tests. Tukey's multiple comparison performed showed the importance of using admixtures, such as metakaolin and silica fume, in achieving reduced permeability in concrete.

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