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Durability of Mortars Modified with Calcined Montmorillonite Clay

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Abstract

This study aims to evaluate the performance of mortars containing locally available Pakistani montmorillonite (Mmt) clay mineral as partial replacement of cement in various curing environments. The local montmorillonite clay in "As is" (20°C) and "heated" (100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C & 1000°C) conditions was incorporated in mortar cubes as partial replacement of cement. Montmorillonite clay of all the temperatures was replaced by 15%, 20%, 25%, 30% and 35% of cement mass in mortar cubes. The Strength Activity Index (SAI) was calculated to determine the optimum activation temperature for the clay. Compressive strengths of the controlled mix and montmorillonite modified mortars were evaluated under the Sodium Sulfate (SS) (5% solution) and mixed (Sodium Sulfate + Sodium Chloride (SCS)) (5% +3.5% solution) curing environments to study its durability performance. Upon thermal treatment montmorillonite clay with 25% cement replacement exhibit competent compression results. Moreover, up on exposure to aggressive environments, montmorillonite clay mortars performed better than the control samples. The mortar cubes exposed to Sulfate environment (SS) were more damaged in compression than that exposed to mixed environment (SCS), for all replacement levels and time exposures.

Keywords: Montmorillonite Clay; Calcined Clay; Corrosive Environment; Sodium Sulfate Environment; Sulfate Attack; Chloride Attack; Durability.

1. Introduction

Concrete and mortar are the most-utilized man made construction materials around the world. These are made from naturally available materials, which made it a famous construction material since long. Beside many advantages durability of concrete and mortar in various corrosive environments are of a primary concern. Concrete durability can be defined as its ability to resist any attack when exposed to different environments [1]. Durability means to meet the requirements of strength, stability and serviceability throughout its service life [2]. For a durable concrete selection of materials and its mix design is of prime importance [3]. The main disadvantage of concrete is its porous micro structure, through which water and other harmful chemical infiltrates that deteriorate the concrete thus damaging its health. Being a permeable material, concrete allows the penetration of harmful agents like acids, alkalis, carbon dioxide and chlorides

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to steel reinforcement bars that causes a complete failure of the structure [4]. Concrete structures exposed to corrosive environments for a long time deteriorate its performance chemically, physically as well as mechanically. The physical deterioration is due to thermal expansion of mortar and aggregates, while the mechanical deterioration is due to cavitation and abrasion of concrete [2, 5]. Chemical deterioration is caused by the penetration of aggressive ions and its interaction with the resultant products of hydration. This interaction of aggressive chemical ions with the hydrated cement phases cause expansion, cracking and spalling of concrete structures [6]. In the aggressive environment concrete deterioration is because of cement matrix dissolution, formation of non-binding phases and expansion [7]. Dissolution causes slackening of concrete microstructure. Expansion of non-binding phases occur relative to substrate phases which initiate the fracture of concrete [7-9].

A lot of research has been carried out on chemical degradation of concrete [10-14]. Sulfate attack is considered one of the crucial factor in the deterioration of concrete. Mechanism of sulfate attack has been investigated by many researchers [8, 9, 12]. Some researchers have concluded that the deterioration of concrete by sulfate attack is due to the penetration of sulfate ions into the concrete and its reaction with the hydrated phases [6, 7, 15]. While others have reported that during the sulfate attack three reactions occur, i.e. ettringite re-crystallization, gypsum formation, decalcification of calcium silicate hydrate (C-S-H) [16, 17]. Numerous theories have been formulated for complex mechanism of sulfate attack, some of which are in confliction [8, 9]. For these reasons, the sulfate attack of concrete has become the field of interest for researchers.

Concrete is vulnerable to the sulfate attack in the sea water or marine environment [1, 18, 19]. Marine environment contain a rich amount of chloride and sulfate ions and is considered a big threat to concrete health [20]. Chloride ions penetrate to concrete causing the corrosion of reinforce steel while the sulfate ions form expansive ettringite and gypsum causing deterioration of concrete health [17, 19]. To address the durability problems in harsh environments, researchers are involved in discovering some supplementary cementitious materials (SCM) as an alternative of cement. Many SCM (silica fume, blast furnace slag, fly ash, metakaolin etc.) are found and replaced with cement by researchers to reduce the attack of aggressive environments on concrete [21-23]. Many modern concrete structures are made using different admixtures and pozzolana to improve the porous structure of concrete and reduce the amount of CH by utilizing it in the pozzolanic reactions. This modification will improve the microstructure and will ultimately enhance the durability and service life of the of cement composites [24]. To modify the cement pozzolana like metakaolin, bentonite, fly ash, bagasse ash etc. are extensively utilized. These pozzolana have rich amount of silica and alumina which have a positive influence on the properties of concrete and mortar. By the utilization of pozzolana the permeability of concrete can be reduced and its resistance to sulfate and chloride attack can be increased [25].

Heated/Calcined clay is considered an effective supplementary cementitious material due to its pozzolanic nature. It has siliceous or siliceous aluminous nature, making it reactive with calcium hydroxide (CH) to form a calcium-silicate-hydrate (C-S-H) gel in the presence of moisture [26]. The performance of cement based materials need to be improved. To fulfil this desire, a lot of pozzolanic materials have been discovered and used in the past study [27-29]. Mixing Ordinary Portland Cement (OPC) with other supplementary pozzolanic materials reduce the penetration of harmful media. Aggressive environments like chlorides, acids, and sulfates cause the degradation of CH obtained during the hydration process of OPC [30, 31]. CH is the most allergic component for the corrosive media. CH is consumed during pozzolanic reaction, thus reducing CH content durability of hydrated cement is improved [32-36]. Due to low heat of hydration pozzolanic incorporated blended cement shows high resistance to thermal cracking. Moreover, these blended cements improve ultimate strength, reduce permeability due to pore refining and enhance resistance to chemical attack and carbonation attack [31, 37, 38].

Demand and use of blended cements have been increasing with time as apart from the mentioned benefits they are low cost, eco-friendly and sustainable [39, 40]. Production of OPC consume more energy and it is hazardous to the environment due the emission of carbon dioxide. Various researches on Pakistani Mmt clay have been carried out to address this issue, however, they did not consider thermal activation of the clay properly. This study investigates the activation of clay at different temperatures for local available montmorillonite clay in Pakistan. The use of heated clay in mortar as partial replacement of cement will enhance its durability properties. Use of heated clay in mortar as partial cement replacement and its effect on the mechanical strength of mortar specimens in the extreme curing environments are the main objectives of this research.

The purpose of this work is to compare the durability of mortars regarding the sulfate attack and chloride penetration, by replacing the OPC with the montmorillonite clay at several replacement levels.

2. Experimental Program

Flow chart of the methodology is shown in the Figure 1.

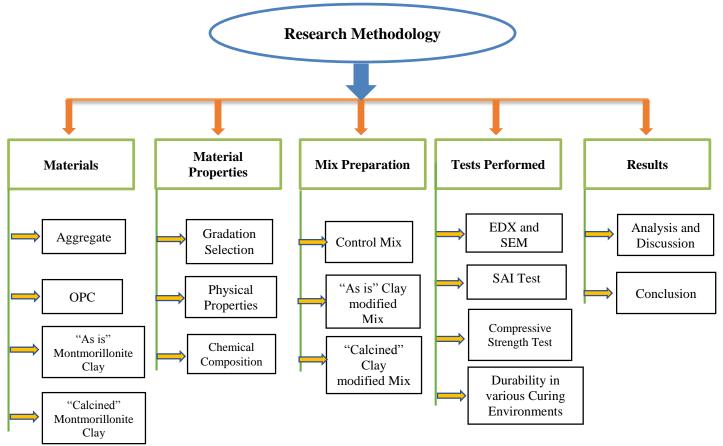


Figure 1. Scope and research methodology

2.1. Materials

All the materials were collected from local resources. Mortar cubes were prepared with locally available ordinary Portland cement (Fauji brand) fulfilling the requirements of ASTM standard C150-07 [41]. Properties of the cement used are given in Table 1 and Table 2. Montmorillonite clay (shown in Figure 3) was taken from Jahangira Sawabi, located at 33° 59' 56'' latitude and 72° 12' 47'' longitude in the survey of Pakistan topographic sheet 43C/1. The clay taken from the source was powdered first, passed through sieve #200 and packed in plastic bags to keep it safe from moisture. Jahangira Montmorillonite clay fulfils the ASTM C618-08 requirements to be used as natural pozzolana. River sand (locally known as Lawrence Pur sand) was used as fine aggregate, having a fineness modulus of 2.3, specific gravity of 2.7 and water absorption of 1.22%. Its particle size distribution as per ASTM C136-06 [42] is given in Figure 2.

Table 1. Physical properties of OPC and Montmorillonite Clay

Physical Properties	OPC	Montmorillonite	ASTM C618 Class N requirements (%)
% Retained #325 mesh	-	11.4	34 max.
Blaine fineness (cm ² g ⁻¹)	3152	2571	
Specific gravity (g cm ⁻³)	3.11	2.42	
Average Particle size	20µm	4 to 5 µm	
Strength Activity Index (%)			
7 day	-	84.4	75 min
28 day	-	85.3	75 min

Chemical Composition (wt. %)	OPC	Montmorillonite	ASTM C618 Class N requirements (%)
Sodium oxide (Na ₂ O)	-	1.39	5 max
Magnesium oxide (MgO)	2.32	2.70	
Aluminum oxide (Al ₂ O ₃)	9.78	18.23	
Silicon dioxide (SiO ₂)	18.8	56.6	
Potassium oxide (K ₂ O)	-	0.67	
Calcium oxide (CaO)	59	3.1	
Titanium oxide (TiO ₂)	-	0.98	
Ferric oxide (Fe ₂ O ₃)	3.44	6.1	
Sulphur tri oxide (SO ₃)	2.85	-	
$(SiO_2)+(Al_2O_3)+(Fe_2O_3)$	-	80.93	70 min
Loss on ignition (LOI)	-	7.1	10 max

Table 2. Chemical composition of OPC and Montmorillonite Clay

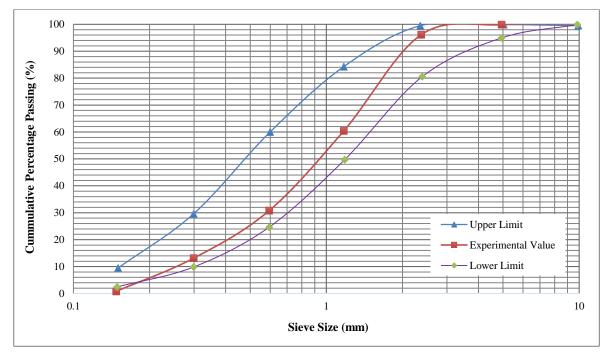


Figure 2. Particle size distribution of fine aggregates

2.2. Heating of Montmorillonite Clay

Mmt clay was heated in a specially designed locally manufactured electric furnace as shown in the Figure 3. For control and uniform burning the temperature was allowed to reach the target limit before placing the clay sample in the furnace. The clay samples were put in the furnace for the required duration. Mmt clay was heated at ten different activation temperatures. The heating temperature range was from 100°C to 1000°C. The clay was heated at 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C each. The heating duration was kept 3 hours. The furnace took 24 hours to reach the room temperature. In the meantime the samples remained placed in the furnace. The clay samples after heating were then packed in PVC bags in order to prevent it from moisture and were placed in the laboratory at room temperature.



Figure 3. Montmorillonite used in the Research, (a) Mmt clay Received after grinding; (b) "As is" Mmt clay; (c) Heating of Mmt clay; (d) "Calcined" (800°C) Mmt clay

2.3. Mix Design, Casting, and Curing of Specimens

For mortar cubes the standard size of $50 \times 50 \times 50$ mm specimens as per ASTM C109 [43] were used for casting and testing. Mixes made were control mix, "As is" Mmt modified mix, and "Calcined" Mmt modified mix as shown in Table 3. Percent by mass replacement levels, for both "As is" and "Calcined" clay, with cement were 15, 20, 25, 30 and 35% each. The cement-to-sand ratio of 1:3 was used with water-to-cement=0.45 for control mortar mix, similarly the water-to-binder (cement + Mmt) ratio of 0.45 was used for the Mmt modified specimens. The entire specimens were tested for the defined ratio of replacement. These samples after demolding were kept in curing tanks as per study plan.

	1
Mix IDs	Description
СМ	Control Mix
MM15	15% Mmt replacement with OPC
MM20	20% Mmt replacement with OPC
MM25	25% Mmt replacement with OPC
MM30	30% Mmt replacement with OPC
MM35	35% Mmt replacement with OPC

Table 3. Mix IDs and description

General ID, for control mix is "CM-E" and for Mmt modified mix is "XMMR-E".

Where, "CM"= Control mix, "X" = heating temperature, "MM" = Montmorillonite clay,

"R" = Percent replacement, "E"= Curing Environment.

2.4. Mortar Cubes Exposed to different Corrosive Environments

The mortar cubes were exposed to three curing environments, 1) Normal Potable Water. 2) 5% Sodium Sulphate Solution. 3) Mixture of 5% Sodium Sulphate and 3.5% Sodium Chloride Solution, as shown in Figure 4, for the period up to 90 days. Sea water contains both sulfate and chloride ions that is why the mortar cubes were exposed to predict its performance in the mixed solution. The mortar cubes after casting were first kept in water for seven days, so that these

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cubes achieve sufficient strength prior to sulfate and chloride attack. The samples were tested after 28, 56 and 90 days each after casing. To keep the concentration stable the solutions were changed every week.



Figure 4. Exposure of samples to different curing environments: (a) Water; (b) Sulfate Solution; (c) Mixed Solution

3. Tests Performed

The tests performed were, EDX and SEM analysis of Mmt clay, Compressive strength of Mmt modified and OPC mortars (ASTM C109, 2007c), Strength activity index (ASTM C618, 2008) and Sulphate + Chloride attack resistance were found. The compression testing machine used was load control having maximum load capacity of 3000 KN, load indication accuracy of $\pm 0.5\%$, oil pump motor of power 0.85 KW. SEM was used to study the topography of the clay particles by firing a focused electron beam across the surface and Energy Dispersive X-Ray analyser (EDX) was used to study the elemental composition of the clay. Apparatus used for SEM and EDX analysis had magnification capacity from 20x to 200,000,0x.

4. Results and Discussion

4.1. EDX and Scanning Electron Microscopy

The EDX analysis both for "As is" and "800°C calcined" Mmt clay is shown in Figures 6 and 8, showing its elemental composition. From the composition analysis it can be seen that $(SiO_2) + (Al_2O_3) + (Fe_2O_3)$ of "As is" Mmt clay is 80.93% and that of "800°C Calcined" Mmt clay is 80.81% which are greater than 70. So both can be used as cement replacement material as per ASTM C618 [44]. Also, the scanning electron microscopy (SEM) was done for both "As is" and "800°C calcined" Mmt clay, SEM images are shown below in Figure 5 and Figure 7. This was done to know about the Mmt clay shape and particle size. From SEM analysis it was found that both "As is" and "800°C calcined" Mmt clay are greater.

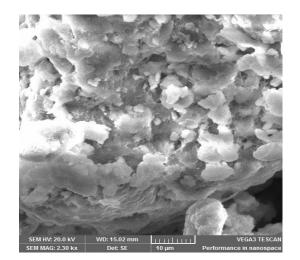


Figure 5. SEM image of "As is" Mmt clay

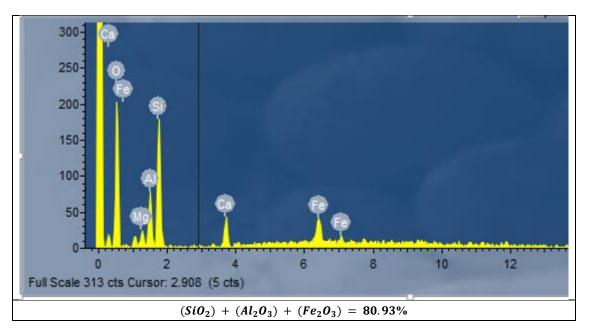


Figure 6. Chemical Composition of "As is" Mmt clay

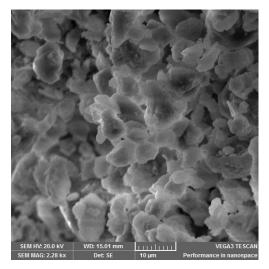


Figure 7. SEM image of "800°C calcined" Mmt clay

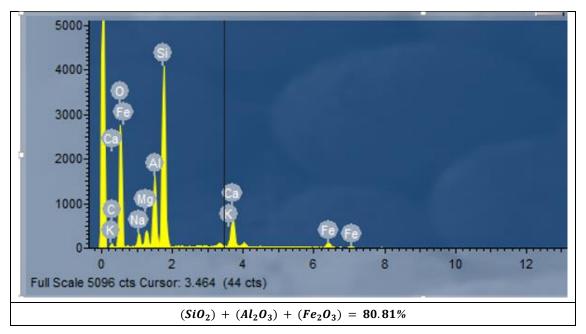


Figure 8. Chemical Composition of "800°C calcined" Mmt clay

4.2. Strength Activity Index

As per ASTM standard C618 strength activity index can be defined as:

$$SAI = \binom{A}{B} \times 100\% \tag{1}$$

Where A = Compressive of OPC mortars containing montmorillonite.

B = Compressive of OPC mortars without montmorillonite.

According to ASTM C618, for any material to be considered as pozzolanic, its SAI should be at least 75% of control mix, both for 7 and 28 days, at its 20 % cement replacement level. In Figure 9, SAI of OPC mortar and that of Mmt modified OPC mortar are shown. All the mortar mixes containing "As is" and "Calcined" Mmt clay fulfill ASTM C618 requirements on due days, except the mixes modified with 900°C and 1000°C calcined Mmt clay. SAI values of mortars modified with "As is" Mmt clay were 82% and 83% on 7 and 28 days respectively. While SAI of "800°C calcined" Mmt modified mortars were 92% and 93.5% on 7 and 28 days respectively. It is higher amongst all the other mixes that is why for the remaining tests "800°C calcined" Mmt clay was selected as a cement replacement. At initial heating from 100°C to 300°C pozzolanic activity was a bit improved as compared to "As is" Mmt modified specimens. This little improvement is due to dehydration, as for Mmt clay dehydration occurs in a temperature range of 150°C to 300°C [45]. Activation temperatures of 700°C and 800°C show much better results amongst all the temperatures as shown in Figure 8. This activation of clay is due to the dehydroxylation phase of Mmt clay, as dehydroxylation of Mmt clay occurs in the temperature range of around 650°C to 850°C [45, 46]. For high temperatures SAI values showed a declination in the pozzolanic reactivity, this declination is due to recrystallization of the clay structure and production of new mineral phases [45, 46].

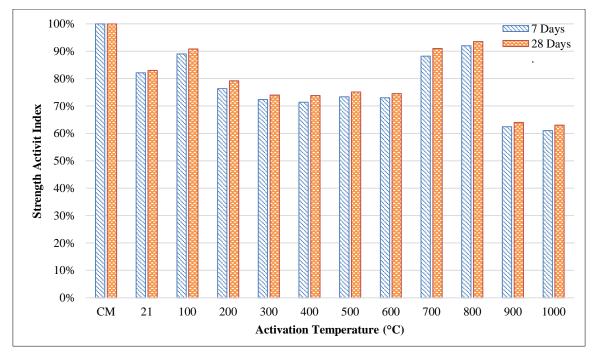


Figure 9. Strength activity indices of CM, "As is" Mmt modified and "Calcined" Mmt modified mortars

4.3. Effect of Normal Curing Water on the Compressive Strength of Mortar Cubes

4.3.1. "As is" Mmt Modified Mortars

Mortar cubes for CM and "As is" Mmt modified mix for the defined replacement level were cast and cured in the potable water for 7, 28, 56 and 90 days. Compressive strength of "As is" Mmt modified mixes was lower than the control mix (CM) at all ages. As the Mmt replacement level was increased, the compressive strength was decreased as shown in Figure 10. However strength was increased with age for both CM and Mmt modified mortar cubes.

Up to 25% replacement decrease was minimum, but at 30% and high proportions of Mmt compressive strength started decreasing progressively. 20% "As is" Mmt modified mortars showed strength of 82% of the CM at 28 days, 83% at 56 days and similarly 85.8% at 90 days. At later ages their strength will get close to CM or may get increase than that of CM as found by [47, 48]. Strength gain rate showed a small gradual increase with age, i.e. the Strength development rate for 28 days was greater than 7 days and that of 56 days was greater than 28 days and so on. It means strength gain

rate for mortar cubes containing pozzolan (Mmt), was slow at early ages but was increased with time, as reported by [26, 47, 48]. This 20% replacement can be used as cement replacement material. Above this replacement level, the compressive strength results were not that much competent as shown.

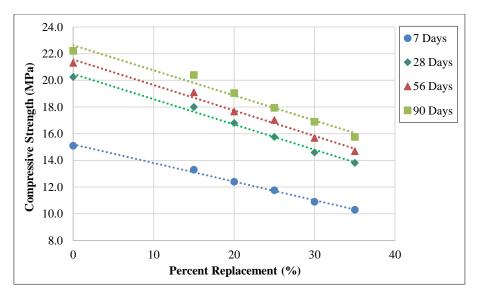


Figure 10. Compressive strength variation of "As is" Mmt modified mortars under water

4.3.2. "800°C Calcined" Mmt Modified Mortars

Mortar cubes for CM and "800°C calcined" Mmt modified mix for the defined replacement level were casted and cured in the potable water for 7, 28, 56 and 90 days. Here too compressive strength of modified mortar cubes at all ages is lower than the control mix (CM). As the Mmt replacement level was increased, the compressive strength got decreased as shown in Figure 11. However, strength values were more satisfactory as compared to "As is" modified mortar cubes. Strength was increased with age for both CM and Mmt modified mortar cubes.

The strength gain rate showed a gradual increase with age as described by [26, 47, 48]. However, in this case the gain rate is better than that of "As is" Mmt modified mortar cubes. Here 20% "800°C calcined" Mmt modified mortars showed a strength of 91.8% of the CM at 28 days, 93.3% at 56 days and similarly 95.9% at 90 days. This improvement of gain rate is due to the activation of Mmt clay with temperature. By heating the clay at an optimum calcined temperature its pozzolanic reactivity can be enhanced/improved as found by [49-52]. With the age gain rate continued to increase progressively with more speed in this case. 25% "800°C calcined" Mmt modified mortars showed a strength of 82.6% of the CM at 28 days, 83.5% at 56 days and similarly 84.7% at 90 days. At later ages their strength will get close to CM or may get increase than that of CM [47, 48]. Thus 25% replacement should be used as cement replacement material as it gave satisfactory results. Above this replacement level, the compressive strength results were not good as shown.

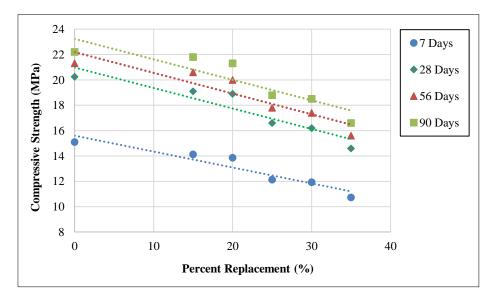


Figure 11. Compressive strength variation of "800°C calcined" Mmt modified mortars under water.

4.4. Effect of Sulfate Solution (SS) on the Compressive Strength of Mortar Cubes

The compressive strength of CM, "As is" Mmt modified and "800°C calcined" Mmt modified mortar cubes immersed in 5 % Na₂SO₄ solution were found for 56 and 90 days. The compressive strength of CM as well as the modified mixes degraded with the time of exposure as shown in Figure 12 & Figure 13. It was found that over all Mmt modified mortars performed better than CM in the sulfate environment. With the time of exposure to sulfate environment control mortar cubes degrade at a fast rate than that of Mmt modified mortar cubes as shown in Fig. 16 and Fig. 17. Moreover, it was observed for 25% replacement, both "As is" and "800°C calcined" Mmt modified samples deteriorate less than control samples and other percent replacement levels of Mmt with OPC. At 90 days the compressive strength was highest for 25% replacement level of both "As is" and "800°C calcined" Mmt modified mixes. This improvement is be due to the micro-filler effect of Mmt clay being a fine-grained material. Excess Mmt above this 25% replacement level is more than the pore filling requirement that causes weakness, which can lead to an increase in sulfate attack, ultimately reducing the compressive strength [50]. This is in line with the findings of other studies [32, 36], that CH is the most allergic component for the corrosive media. CH is consumed during pozzolanic reaction, thus reducing CH content durability of hydrated cement is improved [32-36]. It was also found that the "Calcined" clay modified samples showed more resistance to sulfate attack than that of "As is" clay modified samples as shown.

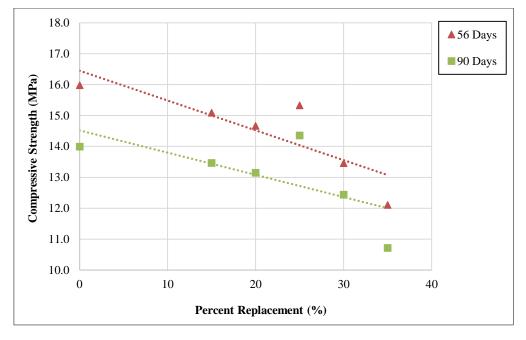


Figure 12. Compressive strength variation of "As is" Mmt modified mortars under Sodium sulfate solution

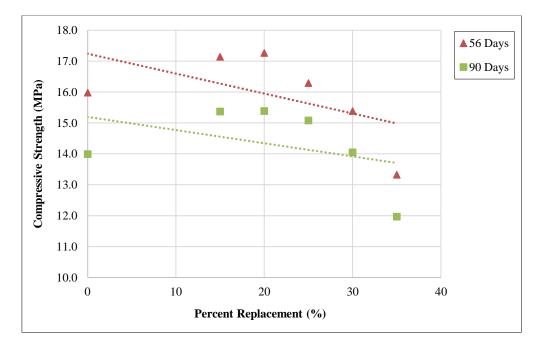


Figure 13. Compressive strength variation of "800°C calcined" Mmt modified mortars under Sodium sulfate solution

4.5. Effect of Mixed (Sulfate + Chloride) Solution (SCS) on the Compressive Strength of Mortar Cubes

The compressive strength of CM, "As is" Mmt modified and "800°C calcined" Mmt modified mortar cubes immersed in mixed (3.5% NaCl + 5% Na₂SO₄) solution were found for 56 and 90 days. Here too, the strength of CM and modified mixes declined with the time of exposure, and in the same way Mmt modified samples was more resistive to the chemical attack as compared to CM samples as shown in Figures 14 and 15. In the same way for 25% replacement level the modified mixes were found more resistive as compared to other replacement levels as discussed. It was seen that, irrespective of the time of exposure and corrosive environment, CM samples are more susceptible to chemical attack than that of Mmt modified mortar samples. This is due to the fact that use of pozzolona clay in mortars led to the production of additional calcium silicate hydrate (CSH) by consuming the hydrated product calcium hydroxide (CH) in the presence of moisture. CH is the main target for corrosive ions, thus reducing CH amount causes a reduction in expansive ettringite and gypsum, ultimately minimize the sulfate attack and chloride attack [32-36].

Furthermore, it was found that in the mixed (SCS) solution compressive strength of both the CM and modified samples were greater than that in sulfate (SS) solution. In the mixed solution, due to the ingress of the chloride ion into sulphoaluminate hydrate the sulfate attack had been restricted up to some extent [53], which retards the formation expansive ettringite and gypsum by producing Freidel's salt.

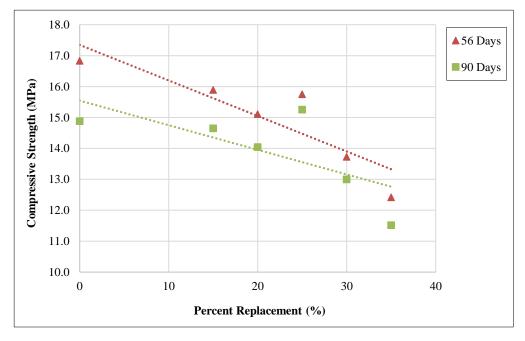


Figure 14. Compressive strength variation of "As is" Mmt modified mortars under mixed (SCS) solution

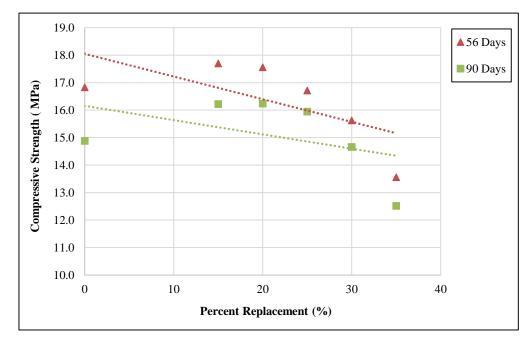


Figure 15. Compressive strength variation of "800°C calcined" Mmt modified mortars under mixed (SCS) solution

4.6. Comparison of Compressive Strength Reduction in Various Environments

After 90 days in SS environment the percent strength reduction of CM, 20% "As is" Mmt modified and 20% "800°C calcined" Mmt modified samples were 37%, 31 and 27.8% respectively as shown in Figures 16 and 17. It is clear that irrespective of curing environment and time of exposure percent strength reduction for "Mmt modified" mixes is less than control mixes. Moreover, percent strength reduction of "Calcined" Mmt modified is less than "As is" Mmt modified mixes. So cement composites can be made durable by using calcined Mmt clay as partial cement replacement material.

From Figures 16 and 17, it can also be noted that after 90 days in SCS environment the percent strength reduction of CM, 20% "As is" Mmt modified and 20% "800°C calcined" Mmt modified samples were 33%, 26.3 and 23.8% respectively. This is showing that irrespective of composition of the mortar, replacement level and time of exposure for all the mixes percent strength reduction in SCS (mixed) environment is less than that in SS environment. From Figure 18 it can be seen that strength reduction of 25% "800°C calcined" Mmt modified mortar mix in SS and SCS was 19% and 15% respectively which is less than the strength reduction of all other mixes. This means that 25% replacement level is the optimum replacement level to produce a durable cement blend. As more CH is consumed during pozzolanic reaction of calcined clay to form additional CSH gel, thus reducing CH content durability of hydrated cement is improved [32-36].

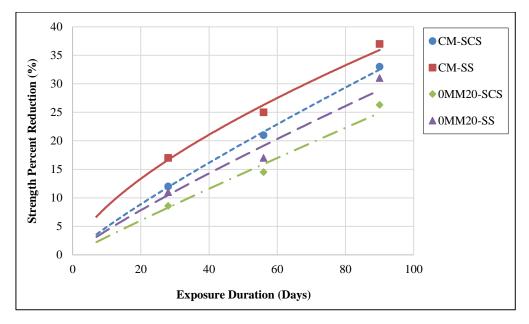


Figure 16. Percent strength reduction of CM and "As is" 20% Mmt modified mortars with age under SS and SCS environment

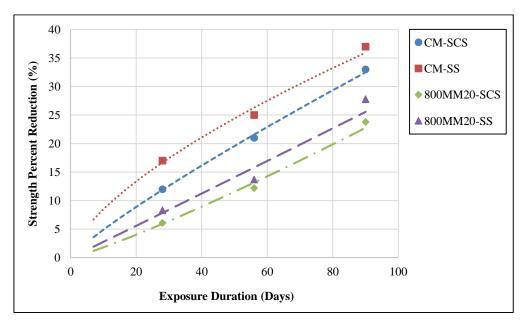


Figure 17. Percent strength reduction of CM and "800°C calcined" 20% Mmt modified mortars with age under SS and SCS environment

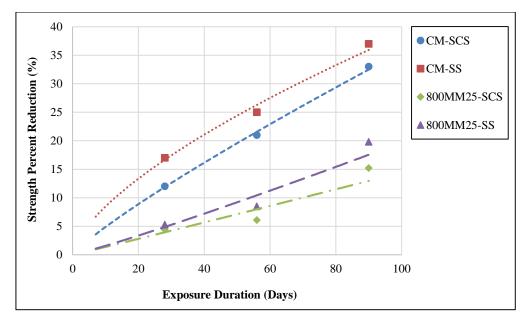


Figure 18. Percent strength reduction of CM and "8000C calcined" 25% Mmt modified mortars with age under SS and SCS environment

5. Conclusion

The experimental study in this paper give an insight to the durability of mortar cubes prepared with thermally activated Pakistani montmorillonite clay as SCM in order to provide a competent cement blend for a durable construction material. The clay was initially heated and then was replaced with cement by different percentages to cast mortar cubes. The control and Mmt modified cubes were cured in different extreme environments and their results were compared with the cubes cured in normal curing water. Based on the experimental results the following conclusions can be drawn:

- 28 day strength activity index values of "As is" Mmt, "100°C calcined" Mmt, "800°C calcined" Mmt and "900°C calcined" Mmt modified mortars were 83%, 90.8%, 93.5% and 64% respectively. This indicated that pozzolanic reactivity of Mmt clay was slightly improved at 100°C activation temperature. However, the maximum activation was occurred at 800°C and notably low reactivity was found at 900°C onward.
- Based upon the compressive strength of the mortars, 20% "As is" Mmt modified mortars showed a strength of 82% and 83% of the strength of control specimens, while 25% "800°C calcined" Mmt modified mortars showed the compressive strength of 80.1% and 82.1% of the control samples on 7 and 28 days respectively. So as per ASTM C618 requirements Pakistani Mmt clay can be used as cement replacement material for durable cement composites.
- After 90 days, 25% "800°C calcined" Mmt modified mortar (800MM25) showed a strength reduction of 19% and 15% of the control specimens in SS and SCS environment respectively which is less than the strength reduction of all other mixes. This demonstrated the effectiveness of Pakistani Mmt clay as SCM for a durable mortar and concrete construction.
- In mixed (SCS) (Sodium sulfate + Sodium chloride) environment intensity of damage was comparatively low than that of SS (Sodium sulfate) environment in all the cases. This conclude that mixed environment is less corrosive as compared to sulfate environment

Based on the results, the local Pakistani montmorillonite clay can be used as SCM in cement and concrete construction. It improves the resistance of cementitious composites to different chemical attacks. In addition it should be noted that to increase the pozzolanic reactivity of the Mmt clay, it needs to be thermally activated.

5. Conflicts of Interest

The authors declare no conflict of interest.

6. References

 Frias, M., S. Goñi, R. García, and R. Vigil de La Villa. "Seawater Effect on Durability of Ternary Cements. Synergy of Chloride and Sulphate Ions." Composites Part B: Engineering 46 (March 2013): 173–178. doi:10.1016/j.compositesb.2012.09.089.

- [2] P. W. Brown and H. F. W. Taylor, "The role of ettringite in external sulfate attack," Materials Science of Concrete: Sulfate Attack Mechanisms, The American Ceramic Society, pp. 73-98, 1999.
- [3] Neville, Adam M., and Jeffrey John Brooks. Concrete technology. England: Longman Scientific & Technical, 1987.
- [4] Nochaiya, Thanongsak, Watcharapong Wongkeo, and Arnon Chaipanich. "Utilization of Fly Ash with Silica Fume and Properties of Portland Cement–fly Ash–silica Fume Concrete." Fuel 89, no. 3 (March 2010): 768–774. doi:10.1016/j.fuel.2009.10.003.
- [5] Leklou, Nordine, Van-Huong Nguyen, and Pierre Mounanga. "The Effect of the Partial Cement Substitution with Fly Ash on Delayed Ettringite Formation in Heat-Cured Mortars." KSCE Journal of Civil Engineering 21, no. 4 (July 7, 2016): 1359–1366. doi:10.1007/s12205-016-0778-9.
- [6] Zhou, Yingwu, Hao Tian, Lili Sui, Feng Xing, and Ningxu Han. "Strength Deterioration of Concrete in Sulfate Environment: An Experimental Study and Theoretical Modeling." Advances in Materials Science and Engineering 2015 (2015): 1–13. doi:10.1155/2015/951209.
- [7] M. Collepardi, "Ettringite formation and sulfate attack on concrete," ACI Special Publications, vol. 200, pp. 21-38, 2001.
- [8] Neville, Adam. "The Confused World of Sulfate Attack on Concrete." Cement and Concrete Research 34, no. 8 (August 2004): 1275–1296. doi:10.1016/j.cemconres.2004.04.004.
- [9] Santhanam, Manu, Menashi D Cohen, and Jan Olek. "Sulfate Attack Research Whither Now?" Cement and Concrete Research 31, no. 6 (May 2001): 845–851. doi:10.1016/s0008-8846(01)00510-5.
- [10] Sun, Chao, Jiankang Chen, Jue Zhu, Minghua Zhang, and Jian Ye. "A New Diffusion Model of Sulfate Ions in Concrete." Construction and Building Materials 39 (February 2013): 39–45. doi:10.1016/j.conbuildmat.2012.05.022.
- [11] Bonakdar, A., B. Mobasher, and N. Chawla. "Diffusivity and Micro-Hardness of Blended Cement Materials Exposed to External Sulfate Attack." Cement and Concrete Composites 34, no. 1 (January 2012): 76–85. doi:10.1016/j.cemconcomp.2011.08.016.
- [12] Idiart, Andrés E., Carlos M. López, and Ignacio Carol. "Chemo-Mechanical Analysis of Concrete Cracking and Degradation Due to External Sulfate Attack: A Meso-Scale Model." Cement and Concrete Composites 33, no. 3 (March 2011): 411–423. doi:10.1016/j.cemconcomp.2010.12.001.
- [13] Lorente, Sylvie, Marie-Pierre Yssorche-Cubaynes, and Jérôme Auger. "Sulfate Transfer through Concrete: Migration and Diffusion Results." Cement and Concrete Composites 33, no. 7 (August 2011): 735–741. doi:10.1016/j.cemconcomp.2011.05.001.
- [14] Tixier, Raphaël, and Barzin Mobasher. "Modeling of damage in cement-based materials subjected to external sulfate attack. II: Comparison with experiments." Journal of materials in civil engineering 15, no. 4 (2003): 314-322. doi: 10.1061/(asce)0899-1561(2003)15:4(314).
- [15] Aït-Mokhtar, Abdelkarim, and Olivier Millet, eds. "Structure Design and Degradation Mechanisms in Coastal Environments" (June 12, 2015). doi:10.1002/9781119006046.
- [16] Lee, Seung-Tae. "Performance of Mortars Exposed to Different Sulfate Concentrations." KSCE Journal of Civil Engineering 16, no. 4 (April 29, 2012): 601–609. doi:10.1007/s12205-012-1054-2.
- [17] Zhang, Minghua, Jiankang Chen, Yunfeng Lv, Dongjie Wang, and Jian Ye. "Study on the Expansion of Concrete Under Attack of Sulfate and Sulfate-chloride Ions." Construction and Building Materials 39 (February 2013): 26–32. doi:10.1016/j.conbuildmat.2012.05.003.
- [18] Jo, Byung Wan, Muhammad Ali Sikandar, Sumit Chakraborty, and Zafar Baloch. "Investigation of the Acid and Sulfate Resistance Performances of Hydrogen-Rich Water Based Mortars." Construction and Building Materials 137 (April 2017): 1– 11. doi:10.1016/j.conbuildmat.2017.01.074.
- [19] Maes, Mathias, and Nele De Belie. "Resistance of Concrete and Mortar Against Combined Attack of Chloride and Sodium Sulphate." Cement and Concrete Composites 53 (October 2014): 59–72. doi:10.1016/j.cemconcomp.2014.06.013.
- [20] Jo, Byung Wan, Sumit Chakraborty, Seung-Tae Lee, and Yun Sung Lee. "Durability Study of Silica Fume-Mortar Exposed to the Combined Sulfate and Chloride-Rich Solution." KSCE Journal of Civil Engineering 23, no. 1 (December 17, 2018): 356– 366. doi:10.1007/s12205-018-5809-2.
- [21] Siddique, Rafat, and Mohammad Iqbal Khan. "Supplementary Cementing Materials." Engineering Materials (2011). doi:10.1007/978-3-642-17866-5.
- [22] Duan, Ping, Zhonghe Shui, Wei Chen, and Chunhua Shen. "Enhancing Microstructure and Durability of Concrete from Ground Granulated Blast Furnace Slag and Metakaolin as Cement Replacement Materials." Journal of Materials Research and Technology 2, no. 1 (January 2013): 52–59. doi:10.1016/j.jmrt.2013.03.010.
- [23] Lee, S.T., H.Y. Moon, and R.N. Swamy. "Sulfate Attack and Role of Silica Fume in Resisting Strength Loss." Cement and Concrete Composites 27, no. 1 (January 2005): 65–76. doi:10.1016/j.cemconcomp.2003.11.003.

- [24] Courard, Luc, Anne Darimont, Marleen Schouterden, Fabrice Ferauche, Xavier Willem, and Robert Degeimbre. "Durability of Mortars Modified with Metakaolin." Cement and Concrete Research 33, no. 9 (September 2003): 1473–1479. doi:10.1016/s0008-8846(03)00090-5.
- [25] Al-Dulaijan, S.U., M. Maslehuddin, M.M. Al-Zahrani, A.M. Sharif, M. Shameem, and M. Ibrahim. "Sulfate Resistance of Plain and Blended Cements Exposed to Varying Concentrations of Sodium Sulfate." Cement and Concrete Composites 25, no. 4–5 (May 2003): 429–437. doi:10.1016/s0958-9465(02)00083-5.
- [26] A. M. Neville, Properties of concrete vol. 4: Longman London, 1995.
- [27] Mwiti, Marangu J., Thiong'o J. Karanja, and Wachira J. Muthengia. "Thermal Resistivity of Chemically Activated Calcined Clays-Based Cements." Calcined Clays for Sustainable Concrete (October 28, 2017): 327–333. doi:10.1007/978-94-024-1207-9_53.
- [28] Provis, John L. "Alkali-Activation of Calcined Clays Past, Present and Future." Calcined Clays for Sustainable Concrete (October 28, 2017): 372–376. doi:10.1007/978-94-024-1207-9_60.
- [29] Martirena, Fernando, Aurélie Favier, and Karen Scrivener, eds. "Calcined Clays for Sustainable Concrete." RILEM Bookseries (2018). doi:10.1007/978-94-024-1207-9.
- [30] Bai, J., S. Wild, and B.B. Sabir. "Chloride Ingress and Strength Loss in Concrete with Different PC-PFA-MK Binder Compositions Exposed to Synthetic Seawater." Cement and Concrete Research 33, no. 3 (March 2003): 353–362. doi:10.1016/s0008-8846(02)00961-4.
- [31] Khan, Muhammad Umar, Shamsad Ahmad, and Husain Jubran Al-Gahtani. "Chloride-Induced Corrosion of Steel in Concrete: An Overview on Chloride Diffusion and Prediction of Corrosion Initiation Time." International Journal of Corrosion 2017 (2017): 1–9. doi:10.1155/2017/5819202.
- [32] Sarfo-Ansah, James, Eugene Atiemo, Kwabena Appiah Boakye, Delali Adjei, and Albert A. Adjaottor. "Calcined Clay Pozzolan as an Admixture to Mitigate the Alkali-Silica Reaction in Concrete." Journal of Materials Science and Chemical Engineering 02, no. 05 (2014): 20–26. doi:10.4236/msce.2014.25004.
- [33] Pierkes, Roland, Simone E. Schulze, and Jörg Rickert. "Durability of Concretes Made with Calcined Clay Composite Cements." Calcined Clays for Sustainable Concrete (October 28, 2017): 366–371. doi:10.1007/978-94-024-1207-9_59.
- [34] Barış, Kübra Ekiz, and Leyla Tanaçan. "Durability of Steam Cured Pozzolanic Mortars at Atmospheric Pressure." Calcined Clays for Sustainable Concrete (October 28, 2017): 46–53. doi:10.1007/978-94-024-1207-9_8.
- [35] Díaz, Ernesto, Raúl González, Dayran Rocha, Adrian Alujas, and Fernando Martirena. "Carbonation of Concrete with Low Carbon Cement LC3 Exposed to Different Environmental Conditions." Calcined Clays for Sustainable Concrete (October 28, 2017): 141–146. doi:10.1007/978-94-024-1207-9_22.
- [36] Maraghechi, H., F. Avet, and K. Scrivener. "Chloride Transport Behavior of LC3 Binders." Calcined Clays for Sustainable Concrete (October 28, 2017): 306–309. doi:10.1007/978-94-024-1207-9_49.
- [37] Berrocal, Carlos G., Karin Lundgren, and Ingemar Löfgren. "Corrosion of Steel Bars Embedded in Fibre Reinforced Concrete Under Chloride Attack: State of the Art." Cement and Concrete Research 80 (February 2016): 69–85. doi:10.1016/j.cemconres.2015.10.006.
- [38] Amin, Noor-ul, Sultan Alam, and Saeed Gul. "Effect of Thermally Activated Clay on Corrosion and Chloride Resistivity of Cement Mortar." Journal of Cleaner Production 111 (January 2016): 155–160. doi:10.1016/j.jclepro.2015.06.097.
- [39] Noor-ul-Amin. "Use of Clay as a Cement Replacement in Mortar and Its Chemical Activation to Reduce the Cost and Emission of Greenhouse Gases." Construction and Building Materials 34 (September 2012): 381–384. doi:10.1016/j.conbuildmat.2012.02.022.
- [40] Ali, Babar, Liaqat Ali Qureshi, Muhammad Asad Nawaz, and Hafiz Muhammad Usman Aslam. "Combined Influence of Fly Ash and Recycled Coarse Aggregates on Strength and Economic Performance of Concrete." Civil Engineering Journal 5, no. 4 (April 28, 2019): 832–844. doi:10.28991/cej-2019-03091292.
- [41] A. Standard, "C150-07," Specification for Portland Cement" (2007). doi:10.1520/c0150-07.
- [42] C. ASTM, "Test Method for Sieve Analysis of Fine and Coarse Aggregates" (2006). doi:10.1520/c0136-01.
- [43] A. Standard, "ASTM C109", "Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-Mm] Cube Specimens)" (2008). doi:10.1520/c0109_c0109m-13.
- [44] C. ASTM, "Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete" (2012). doi:10.1520/c0618-01.
- [45] Snellings, R., G. Mertens, and J. Elsen. "Supplementary Cementitious Materials." Reviews in Mineralogy and Geochemistry 74, no. 1 (January 1, 2012): 211–278. doi:10.2138/rmg.2012.74.6.

- [46] Swamy, R. Narayan, and R. N. Swamy. Cement replacement materials. Vol. 3. Sheffield: Surrey University Press, 1986.
- [47] Mehta, P. Kumar. "Role of pozzolanic and cementious material in sustainable development of the concrete industry." Special Publication 178 (1998): 1-20.
- [48] Mehta, P.K. "Studies on Blended Portland Cements Containing Santorin Earth." Cement and Concrete Research 11, no. 4 (July 1981): 507–518. doi:10.1016/0008-8846(81)90080-6.
- [49] Mirza, J., M. Riaz, A. Naseer, F. Rehman, A.N. Khan, and Q. Ali. "Pakistani Bentonite in Mortars and Concrete as Low Cost Construction Material." Applied Clay Science 45, no. 4 (August 2009): 220–226. doi:10.1016/j.clay.2009.06.011.
- [50] Ahmad, S., S. A. Barbhuiya, A. Elahi, and J. Iqbal. "Effect of Pakistani Bentonite on Properties of Mortar and Concrete." Clay Minerals 46, no. 1 (March 2011): 85–92. doi:10.1180/claymin.2011.046.1.85.
- [51] Tironi, Alejandra, Monica A. Trezza, Alberto N. Scian, and Edgardo F. Irassar. "Assessment of Pozzolanic Activity of Different Calcined Clays." Cement and Concrete Composites 37 (March 2013): 319–327. doi:10.1016/j.cemconcomp.2013.01.002.
- [52] He, Changling, Emil Makovicky, and Bjarne Osbaeck. "Thermal Treatment and Pozzolanic Activity of Na- and Ca-Montmorillonite." Applied Clay Science 10, no. 5 (January 1996): 351–368. doi:10.1016/0169-1317(95)00037-2.
- [53] Ogawa, K., and D.M. Roy. "C4A3S Hydration, Ettringite Formation, and Its Expansion Mechanism: III. Effect of CaO, NaOH and NaCl; Conclusions." Cement and Concrete Research 12, no. 2 (March 1982): 247–256. doi:10.1016/0008-8846(82)90011-4.