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Assessment of pozzolanic activity of thermally activated clay and its impact on strength development in cement mortar

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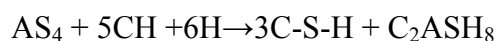
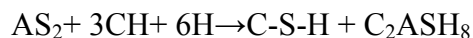
Abstract

Natural kaolinitic clay from Khyber Pakhtoonkhwa, Pakistan was thermally activated at different temperatures and its pozzolonic behavior was studied. Thermal activation was carried out in an electrical muffle furnace at 200, 400, 600 and 800 °C for two hours. The index of order/disorder and structural changes with thermal treatment were studied using X-ray diffraction (XRD) and Fourier transformed infra-red spectrometry (FTIR). The pozzolonic behavior of all the samples was evaluated using electrical conductivity test, lime consumption (LC) test and strength activity index (SAI). This study confirmed that natural kaolinitic clay other than pure kaolinite can act as an interesting pozzolona when thermally activated. The best temperature for thermal treatment of natural kaolinitic clay is 800°C, while the permissible replacement in mortar is 25% as confirmed from the compressive strength measurement.

Key words; Clay, Thermal activation, pozzolonic activity, Electrical conductivity, compressive strength, strength activity index

1. Introduction.

A number of problems are associated with the traditional supplementary materials due to their limited availability or unapproachable location, causing a great economical and environmental impact during their transport. Therefore research for new supplementary materials and their pozzolanic activity is being very much encouraged [1]. One of the newly developed supplementary cementitious materials is the thermally activated clay which is considered as the most important topic of today's cement researchers and cement producers [2]. Thermally treated clays from different origin on a global scale have been studied and characterized for their use in cement [3]. Natural clay deposits may contain a number of different types of clay minerals like kaolinite, illite, montmorillonite, palygorskite, etc. With a variety of different impurities of non clay materials, including quartz, calcite, feldspars, mica, anatase and sulfides [4]. Some of the clay minerals like kaolin and montmorillonites may contain the highest pozzolanic activity, while others even after thermal treatment may or may not have pozzolanic activity [5-6]. Dehydroxylation of argillaceous minerals in the clays on thermal treatment give amorphous phases of aluminosilicate of AS₂ and AS₄ type which react with calcium hydroxide (CH) in the presence of water and give a cementing phase like calcium silicate hydrate (C-S-H) along with some hydrates of alumina bearing phase [7-8]. The proposed pozzolonic reactions are given as follows:



Where AS₂ stands for (Al₂O₃)₂(SiO₂), AS₄ for (Al₂O₃)₄(SiO₂) both are amorphous aluminosilicates, CH for calcium hydroxide, H for water, C-S-H for Calcium silicate

hydrate and C_2ASH_8 for calcium alumino silicate hydrate phase. In measuring the pozzolanic reactivity of calcined clay, the optimum conditions for thermal treatment like temperature, heating time and cooling down rate etc. the activation of different clays is assessed. The assessment of pozzolonic activity is measured by direct methods as well as indirect methods [9-11]. The direct method involves Frattini test, XRD and TGA. In the Frattini test, CH consumption by the active pozzolona during the reaction is measured using titration method. The indirect method measure a change of property related with the pozzolanic reaction such as compressive strength, strength activity index and electrical conductivity.

Frattini test accurately defines the pozzolanic reactivity of blended Portland cements. The source of consumed Calcium Hydroxide is the hydration of pozzolana in Portland cement. This test is very sensible to the chemical characteristic of pozzolan and the alumina content of Portland cement used. In contrast the saturated lime test cannot provide reliable results [5,12]. Among the indirect methods for the measurement of pozzolonic reactivity, the most popular is the strength activity index (SAI) which measures the effect of the pozzolanic reaction on densification of cementing matrix, and packing effect which improves the compressive strength. The mechanism of the test depends upon the change in water-to-binder ratio (w/b) for sample having the same consistency and the proportion of blends and then change in water to binder ratio with the replacement of cement by supplementary cementitious materials. Another indirect test is based on the change in electrical conductivity of pozzolanic material which is dispersed in a saturated solution of lime as reported by Luxan et al. [13], and later on modified by Yu et al. [14] and Payá et al. [15]. This method was later applied to the Portland cement

solution by Sinthaworn and Nimityongskul [16]. The experiment has been applied to different types of other complementary committing additive substances and the correlation between the results has been investigated and reported [17], but such experiments have not been comprehensively applied to different types of thermally treated clays. This study deals with different test methods to assess the pozzolanic activity of the clay, calcined at different temperature and also to find out the maximum amount of clay which can be added to cement mortar. The pozzolanic activity of clay calcined at different temperatures was investigated by one direct test like saturated lime test and two indirect tests like strength activity index and electrical conductivity.

The purpose of this study is to thermally activate the locally available kaolinite clay at different temperatures in order to optimize the activation temperature and study its pozzolonic activity by different ways. The main parameter in natural kaolinitic clay controlling its pozzolanic activity at post thermal treatment was studied using different analytical techniques. The pozzolanic reactivity of clay illustrated excellent relationship with the conversion of kaolinitic content into metakaolinite as determined by FTIR, XRD, electrical conductivity and compressive strength index.

2. Experimental

2.1. Characterization of materials

Natural clay used in this study was obtained from different locations of KPK Pakistan. Chemical composition, as determined by XRF and loss on ignition of clay is given in Table 1. X-ray diffraction (XRD) and Fourier transformed infra-red spectrometry (FTIR) were used to study the mineralogical composition of clay. A Philips PW 3710 diffractometer operating with Cu Ka radiation at 40 KV and 20 mA and Nicolet

Magna 500 spectrophotometer ranged from 4000 to 400 cm^{-1} were used for XRD and FTIR spectrum analysis respectively. kaolinite content (K) was estimated from the XRD peaks and FTIR spectrum.

A normal Portland cement (PC) as shown in table 2 was used for pozzolanic activity tests. The mineralogical composition calculated using the Bogue's formula was $\text{C}_3\text{S} = 60.83\%$, $\text{C}_2\text{S} = 11.17\%$, $\text{C}_3\text{A} = 5.2\%$ and $\text{C}_4\text{AF} = 12.10\%$. This PC has a strength class of 40 (standard compressive strength 8500 PSI at 28 days) and its Blaine specific surface was 2852 sq cm/gram .

2.2. Thermal treatment and characterization of calcined clay.

The particle size of the sample was reduced to smaller than 4 mm. For the thermal treatment a programmable laboratory furnace working up to 1200 $^{\circ}\text{C}$ was used. Four samples of the same clay were heated from the ambient temperature up to 200, 400, 600 and 800 $^{\circ}\text{C}$, and were named as C_{200} , C_{400} , C_{600} and C_{800} respectively while the sample without thermal treatment was named as C_{AR} . The heating rate was set at 15 $^{\circ}\text{C}$ per minute and the time of residence at high temperature was 2 hours. After cooling, the treated clays were ground in a disk grinder until 100% of mass passed through the 45 μm sieves. The treated samples were characterized using XRD and FTIR to study the mineralogical change as a result of thermal treatment. Specific surface area of the calcined clay was studied using the Blaine method as per ASTM C 204-04 standard [18].

2.3. Study of Pozzolanic behavior

Pozzolanic behavior of all the clay samples was studied by two methods

2.3.1. Electrical conductivity:

Electrical conductivity was carried out following the procedure by Qijun et al. [19] in which 2 g of calcined clay was added to 20 ml of concentrated solution of calcium hydroxide at 40 °C and electrical conductivity was measured after regular intervals of time, using a conductivity meter.

2.3.2. Lime consumption test (LC)

In this test, the Ca(OH)_2 consumption in the saturated lime solution containing clay as a suspension is analyzed at different ages. Saturated solution of Ca(OH)_2 was prepared at $40 \pm 1^\circ\text{C}$ and filtered off. 2.5 g of calcined clay was added in 25 ml of a saturated solution. These suspensions were maintained at $40 \pm 1^\circ\text{C}$ until 7, 14, 21, 28 and 35 days. The suspension was filtered off and the filtrate was titrated using HCl 0.02 M to determine the [CH] in solution. The ratio of [CH] obtained from the solution in contact with calcined clay to the [CH]₀ at initial time was expressed as LC.

2.3.3. Compressive strength and strength activity index:

Compressive strength was measured following the procedure Alejandra et al [20] on mortar cubes of 25x25x25 mm made with a blend to sand (1:3) and a water/cementing material ratio of 0.50. The cementing blends were of 25 mass% of ground, calcined clay and 70% Pure Portland cement. The specimens were cured in the molds in a moist curing room for 24 h and then immersed in lime saturated water until test age at $20 \pm 1^\circ\text{C}$. The compressive strength was measured at 3, 7 and 28 days, as the average of three specimens using universal compressive strength testing machine.

The strength activity index was also calculated as the ratio of compressive strength of blended cement of the treated clay samples to the strength of the Portland cement at the same age.

2.2.6. Optimization of thermal temperature and clay replacement.

Thermally activated clay at different temperatures was blended with cement and compressive strength was measured after 3, 7 and 28 days. The amount of clay in all the samples was kept constant as 30%. The optimum temperature was selected from the maximum compressive strength.

For the optimization of clay amount in blends, thermally treated clay at optimum temperature was used in mortar in different percentages like 0, 5, 10, 15, 20, 25 and 30% and was called C₀, C₅, C₁₀, C₁₅, C₂₀, C₂₅ and C₃₀ respectively. Compressive strength was measured in the same way. Clay treated on other temperatures than the optimum one was not used for further study.

3. Results and discussion

3.1. Characterization of materials

XRD patterns of as received clay (Fig. 1a) shows a peak of very strong intensity for kaolinite (K), and a low intensity for quartz (Q). XRD reveals a poor intensity peak of other phases which have not been identified. The peak structure and the wideness indicate that the clay under study has a disordered crystalline structure.

The FTIR spectrum of as received sample is shown in Fig. 2a, which gives a qualitative and quantitative aspects of the order and disorder of the structure, depending on the relative intensity of the OH band in the range of 3600-3700 cm⁻¹ [21]. H₂O stretching was also found at 1643 cm⁻¹. Bands at 1115 cm⁻¹ and 995 cm⁻¹ are assigned to Si-O bonds in the SiO₄ molecules. In the FTIR spectrums of kaolinite, the band near 3620 cm⁻¹ and 3680 cm⁻¹ arise from the internal OH groups and internal surface OH groups respectively. The OH stretching region gives an idea of the structural dis-ordernes. The

bands at 3620 cm^{-1} and 3680 cm^{-1} bands are basically unchanged, but some times doublet is replaced by a single broadband at 3660 cm^{-1} [22]. To find out the order/disorder of kaolinite structure quantitatively, the P° index was calculated as the ratio of intensities of the bands at 3620 cm^{-1} and 3680 cm^{-1} , which is given in Table 3. Kaolinitic clay is considered a well-ordered structure, when P° index is higher than 1 [23]. The table shows that the studied clay has P° index lower than 1, and is a dis-ordered kaolinite structure.

3.2. Calcined clays

X-ray Diffraction patterns of calcined clay samples at different temperatures is shown in Fig. 1b which show that peaks corresponding to kaolinite almost disappear for sample calcined at 800°C . This shows that thermal treatment at 800°C is adequate for the complete conversion of kaolin into metakaolin. This indicates that this temperature is sufficient for the complete conversion of kaolin into amorphous material.

FTIR spectrum of calcined clay at 800°C is shown in Fig. 2b. From the spectrum, it is evident that detectable -OH bands disappears as present in the spectrum of as received sample. The Si-O characteristic bands of kaolinite present in the raw clay transforms to a single absorption band in the heated clay, which is characteristic of the amorphous silica. The H_2O stretching at 1643 cm^{-1} was absent after the thermal treatment. A band of kaolin at 1115 cm^{-1} shifted to lower frequency at 1030 cm^{-1} , which was the amorphous SiO_2 . All these changes are in close agreement to finding of Chakchouk et al. [24]. From both XRD and FTIR analyses, it is confirmed that the transformation of kaolinite into reactive amorphous phase occur by thermal activation.

3.4. Pozzolan activity

Fig. 3 shows the electrical conductivity of calcined clay in lime solution as a function of time. In the first 30 min, a drop of electrical conductivity of lime-solution occurs owing to high utilization rate of Ca^{2+} and OH^- ions, which is attributed to the fixation of dissolved $\text{Ca}(\text{OH})_2$ by calcined clay particles [25]. This performance indicates the reactivity of activated clay (pozzolan) with Calcium hydroxide and is a measure of its pozzolonic activity. The reactivity of clays is indicated from the measure of the drop of electrical conductivity. The drop of electrical conductivity of calcined clay at higher temperature was greater than that of lower temperature. The sample calcined at a higher temperature (800 °C) showed an even lower reactivity than that of calcined at 200, 400 and 600 °C.

The lime consumption with curing time for the Calcined clay at 800°C is shown in Fig. 4. On the first day, C_{800} presents a significant LC representing its immense reactivity, while $\text{C}_{\text{AR}}\text{-C}_{600}$ shows very low LC and comparatively low pozzolonic activity. At 7 days, $\text{C}_{\text{AR}}\text{-C}_{400}$ utilized up to 90% while C_{600} consumed less than 80% of CH. At 14 days, C_{800} attains uniformity in the consumption of LC while all the other clays may cause fall of CH in the remaining solution. Further up to the end of the test all the clay consume more than 90% of CH with the exception of C_{AR} which consume at the most 80% of the CH.

Pozzolonic activity of the studied calcined clay using saturated lime test with the specific surface is shown in Fig. 5. It is observed that with the increase in specific surface area of the calcined clay the consumption of CH was significantly increased. The reaction rate of C_{800} with 1000 m^2/kg is slower than that with 2000 m^2/kg which may be attributed to the specific surface area. Finally pozzolonic activity of clay depends on the nature,

crystallinity, calcination temperature, type and mineralogy of the cement and clay replacement level in mortar.

Compressive strength of ordinary Portland cement mortar (Blank) and blended mortars containing 30% activated clay replacement treated at different temperature and their strength activity index (SAI) is shown in Table 4. It can be seen that water to cement ratio increases with increase of clay in mortar. For a mortar with 30% clay substitution, the dilution factor is corresponding to an increase of the water to cement ratio of 0.5 to 0.71, which may decrease a compressive strength. With the increase in calcination temperature the compressive strength and the SAI increases. When calcined clay at 800°C is integrated in cement mortar, the increase in SAI may be accredited to reaction of active phases with the CH produced as a result of cement hydration. This can be observed that addition of clay causes an increase in the compressive strength (SAI > 1.00) at the curing age of 7 days. After 28 days, mortar having 30% clay activated at 800°C has a further increase in SAI, more than 1.00, whereas the clay treated at 600°C presented SAI lower than 1.00, but still higher than 0.75, on the basis of which it can be considered as active pozzolan. Other clay samples treated at lower temperatures has SAI even lower than 0.75, so the contribution of pozzolanic reaction in mortar cannot recompense for the replacement of cement from blended mortar. From these results it can be concluded that the clay treated at 800°C may be considered as active pozzolona but only clay with 800°C increases compressive strength from the control so the optimum temperature for the calcination of clay under study is 800°C.

Compressive strength of blended cement mortars with different replacement of clay treated at 800°C and their strength activity index is given in table 5. Compressive

strength and strength activity index increase with the increase of replacement level, but the increase is not uniform as clear from table 5. The increase is uniform upto 25% and then a decrease was observed on 30% replacement. The increase upto 25% is attributed to the pozzolonic reactions carried out in the cement blend while the decrease with further increase of clay is because that the release of calcium hydroxide becomes limited in comparison to the amount of clay in the pozzolonic reaction and the unreacted clay decreases the concentration of cement in the blended mortar. It is concluded that the optimum amount of clay which is to be used in blended mortar is 25% treated at 800°C.

Metakaolinite content in activated clay is the main factor which mainly affects the development of compressive strength according to Badogiannis et al. [26]. Similarly Habert et al. [27] concluded that compressive strength is mainly associated with the quantity of activated clay rather than the nature of the clay. The structural and physical parameters of the clay also affect the compressive strength which is the direct indication of the rate of the pozzolanic reaction of Metakaoline. The degree of structural disorder (P°) has a main contribution in the compressive strength. The compressive strength at 7 and 28 days will be approximately 3.0 and 9.0 MPa respectively, when P° changes from 1.10 to 0.50.

XRD pattern of Portland cement mortar after 28 days and that of blended mortar with 25% calcined clay at 800°C, is shown in Fig. 6a and 6b respectively. Fig 6a shows a sharp peak for the presence of calcium hydroxide represented by CH which is released during the hydration of alite and belite in cement. The same peak disappears in Fig. 6b which shows that the released lime during hydration has been consumed by activated clay

during pozzolonic reaction. The purpose of this test is to show that thermally activated clay is active pozzolona and 25% of clay can be blended with cement in mortar.

The nature and compactness of the hydration products formed, especially Calcium silicate hydrate (C-S-H), during the pozzolonic reaction has a deep relationship with the compressive strength of blended mortar. In case of calcined clay, the alumina phases ($C_3A.CH.H_{12}$) is formed which utilize great amount of CH and contribute very little to the compressive strength [28]. The development of compressive strength of blended mortar also depends on the pore size refinement by filling due to the formation of calcium silicate hydrate (C-S-H) or calcium alumino silicate hydrate (C-A-S-H). The accumulation of alumina phase mainly depends on the ratio of CH to Al [29] as well as the temperature for curing [30].

4. Conclusions

Local clay samples after thermal treatment at 800 °C has been proved as the best pozzolana, when mixed in mortar at 25% gave good compressive strength. The strength activity index, lime consumption and electrical conductivity were proved to be the most reliable techniques to evaluate the pozzolonicity of clay. Due to the alumina and silica in clay a large proportion of CH is consumed during LC and EC tests and can lead to overestimating the pozzolonic activity of activated clay in association with the SAI results which show good engine performance of the blended mortar. At different ages, the compressive strength of blended mortar depends on the amount of clay added and the activation temperature. From all the experiments, it may be concluded that the compressive strength of blended cement containing 25% of thermally treated clay at 800 °C showed a very high level of compressive strength which can reduce the cost of

production of cement and greenhouse gases making the cement production as environmentally friendly.

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