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Conversion of Low Cost Mineral Material to Pozzolana and its Impact on Cement Parameters and Cost of Production

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Cement manufacturing is an energy intensive process. Due to global energy crisis and limited resources of fossil fuels, cement manufacturers are under stress for maintaining the sustainability of cement manufacturing. The research has been focused on the addition of pozzolanic material with cement clinker to reduce the energy consumption. In the present study, a locally available mineral material has been investigated for use as a pozzolana with cement. The material has been tested for mixing with cement in different blends i.e. 5 %, 10 %, 15 % and 20 % without treatment and with thermal activation at 200, 400, 600 and 800 °C. The mineralogical composition and phase identification were analyzed by XRF, FTIR, XRD and TGA, while mechanical properties were tested by Vicat apparatus, Blaine air permeability and Universal testing Machine (UTM). It has been found that the locally available mineral material can be mixed with cement clinker upto maximum of 15 %, if thermally activated at 600 °C.

1. Introduction

The cement manufacturers are trying to reduce the cost of production by using alternative fuels or alternative raw materials. Alternative fuels reduce the costs but causes environmental problems. When the pozzolanic materials is grounded and added with clinker up to some proportion, it show cementitious properties (Andrzej, 2009) and reduces the energy consumption and need of raw material for burning during cement production which also reduces carbon emissions. Pozzolanic materials consist of siliceous or siliceous and aluminous materials, which themselves have little or no cementitious property, but finely disperse in the existence of moisture content and it reacts chemically with calcium hydroxide at ordinary temperatures to form compounds that possessing cementitious property (Grilo et al, 2014).
Pozzolanic materials are available either naturally such as volcanic ash, volcanic pumice, shales or tuff or artificially i.e fly ash, blast furnace slag, rice husk ash or calcined clay (Singh, 2006). They are used as an additive/partial replacement with an ordinary portland cement. SiO_2 of the pozzolanic material reacts with free lime of cement to produce supplementary calcium silicate hydrates (CSH), which enhances the properties of compact mass after hydration (Demirbas and Aslan, 1998). The replacement of cement with pozzolana can be increased if the pozzolanic material is activated. Different techniques for the activation of pozzolanic material were developed by researchers such as mechanical activation (Prolong grinding time), Thermal activation and chemical activation (Amin, 2010). Thermal activation is the physical technique in which the clay minerals are treated at high temperature that removes inorganic material and moisture associated with clay (Steudel et al, 2009). The clay having kaolin group is transformed to metakaolin by heat treatment at temperature of 550 to 900 °C in order to remove hydroxyl group and increases the amorphous nature of aluminosilicate compound (Janotka et al., 2010) which is responsible for strong pozzolanic activity (Badogiannis et al, 2005).
The aim of present study is to determine the possibility of using the mineral material deposits, available, 23 km south of Peshawar, Pakistan (approximately 2.7 x 1,011 metric tons) as an additives/partial replacement with cement clinker as pozzolana and further increasing its pozzolanic activity by thermal activation This will results in reduction of raw material requirements and its processing which

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consequently will reduce the energy consumption of cement manufacturing and carbon dioxide emission will also be reduced.

2. Materials and methods

In the present investigation, the locally available mineral material, from Mattani Azakhel Khyber Pukhtoon khwa (Pakistan) has used as an admixture/partial replacement to reveals the major constituents present in the material as pozzolana. The experimental analysis is categorized thermally, mineralogically and mechanically. The cement used in this study as a control was collected from the local market of commercial brand.

2.1 Sample Preparation

Different samples of mineral material were collected from different locations of the study area, spread in the area of 100 km^2. The samples were homogenized in order to study the composition, properties and their effect as a pozzolana with an ordinary Portland cement. The samples were heated at 105 °C for 4 hours in order to reduce the moisture content. The samples used for further processing were screened in a sieve shaker to the desired size (200 mesh).

2.2 Thermal activation

The collected clay samples were thermally activated at different temperatures i.e. 200, 400, 600 and 800 °C using muffle furnace in order to enhance their pozzolanic behaviour and were named as M_{200}, M_{400}, M_{600} and M_{800} respectively. The untreated clay sample was named as $M_{AR.}$

2.3 Preparation of blends

All clay samples including the as received one were blended with commercial cement in different proportions i.e. 5, 10, 15, and 20 % by mass. The pure cement without clay was used as a control.

2.4 Characterization

All samples including the untreated were studied using different analytical techniques like XRF, FTIR and XRD. XRF was performed to study the elemental composition of the studied samples. Fourier Transform Infra red spectroscopy (FTIR) and X-ray diffraction (XRD) were used for structural and phase identification of mineral material for all samples. A wide range IR spectral material KBr (48800) were used in the preparation of sample for FTIR pellet.

Thermo gravimetric analysis (TGA) was performed in the range of 30 to 1,000 °C with a temperature rate of 10.0 °C/min and hold for one minute at 30 °C in order to find the optimum temperature for thermal activation. The blended cement samples were studied for different physical parameters including compressive strength, setting time, Blaine and consistency as per ASTM standards.

3. Results and Discussions

3.1 Chemical/Mineralogical analysis

Table 1 shows the composition of the locally available mineral material (LAMM). The aggregate percentage of the SiO_2+Al_2O_3+Fe_2O_3 is 77.85 %, greater than 70 %, which indicate the possibility of pozzolanic activity in the material (Alp et al, 2009).Therefore, the material was then processed for further testing.

Table 1: Concentration Analysis (XRF) of locally available Mineral Material

Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI
Percentage	54.98	17.54	5.33	5.40	0.20	0.00	0.95	0.09	14.50

The LAMM, “as received” and activated samples were blended with the ordinary Portland cement (OPC) to know the effect and change in the composition of OPC, which have shown in Table 2. The combination of the major four components SiO_2, Al_2O_3, Fe_2O_3 and CaO in all cases is more than 90 %, which fulfill the requirements of pozzolanic cement. It can be observed that both, the increase in blending proportions and activation temperature increases the SiO_2 and Al_2O_3 while the percentage of Fe_2O_3 and CaO decreases as the activation temperature increases because the iron oxide II and III (FeO and Fe_2O_3) is converted to alpha phase of iron, α-Fe and form hematite in the temperature range of 500 – 700 °C, whereas at 400 °C, Fe_2O_3 reacts with hydrogen and change their phase to magnetite. Lime (CaO) is an inorganic material which is found in the form of oxide and hydroxides and carbonates of alumino-silicates, and iron existing

materials. CaO is fused with other minerals like aluminium oxide, ferric oxide and silicate in the range of temperatures from 25 – 900 °C.

Table 2: Composition of Cement, blended with different proportions of LAMM at different activated temperatures

Blending,%	AR	200 °C	400 °C	600 °C	800 °C
		SiO_2 (range: 17 - 25 %)			
5	21.76	21.73	21.82	21.88	21.93
10	23.93	23.56	23.75	23.87	23.96
15	26.06	25.39	25.67	25.85	25.99
20	28.28	27.23	27.6	27.83	28.02
		Al_2O_3 (range: 3 - 7 %)			
5	5.18	5.32	5.36	5.38	5.42
10	5.9	6	6.1	6.12	6.2
15	6.62	6.69	6.83	6.87	6.99
20	7.38	7.37	7.57	7.62	7.77
		Fe2O3 (range: 3 - 5 %)			
5	4.12	4	4.01	4.02	4.02
10	4.14	4.03	4.03	4.05	4.06
15	4.25	4.05	4.06	4.09	4.1
20	4.28	4.07	4.08	4.12	4.13
		CaO (range: 60 - 66 %)			
5	59.91	59.51	59.51	59.51	59.5
10	56.55	56.64	56.64	56.63	56.62
15	53.34	53.77	53.77	53.76	53.74
20	50.1	50.9	50.9	50.88	50.86

The low water requirement was found as SiO_2 amount increased while the calcium oxide reduced by the addition of LAMM.

3.2 Fourier Transform infrared Spectroscopy

The results of FTIR spectroscopy of LAMM is shown in figure 1. The received sample shows the IR bands at 3603, 3344.6 and 1631.78 cm-1 which corresponds to the hydroxyl group of H-O-H stretching and Al-O-H stretching while the IR bands at 1006.84, 914,840.96, 783, 732.79, 551.64 cm-1 confirmed the presence of Si–O–Si, Si–O, Al–O–H Str. The IR band of the LAMM samples shows Si-O-Si, Si-O-Al, Si-OH, Si-O-Fe, Al-O-H stretching band and O-Si-O bending band. The IR bands of M_{AR} sample i.e. 3603.03, 3344, 1006.84, 914.26, 783.10, 551.64 cm-1, indicates the presence of kaolinite group which can be confirmed with the results of Preeti et al. [72]. At the activation temperature from 400 to 600 °C, it was observed that the main constituents of the material as required for pozzolonicity like SiO_2, Al_2O_3, and Fe_2O_3 were merged and created new phases like Sillimanite (Al_2SiO_2), Aluminum oxide, Maghemite-C, Corundum (Al_2O_3) and Al_8Fe_2Si were identified at the intensities of 1133, 1195,895, 783 and 1217.

As the temperature increased up to 800 °C only the silicon dioxide was high up in the region upto 300 (2θ) and observed at a d-value of 6.458, 5.227 and 3.190 having the 2θ of 13.70, 16.950 and 27.950 while the other phase as identified at a low temperature activation were rare or unidentified at 800 °C.

3.3 Thermo Gravimeter Analysis (TGA)

The difference in weight (mg) with respect to temperature was measured through Thermo gravimetric analyzer for all samples and the results are shown in Figure 2. It can be seen that the apparent weight loss of the samples M_{AR}, M_{200} and M_{400} are high while the samples activated at M_{600} have a small change

in its weight and almost no change for M_{800}. It can be concluded from the figure 2 that the free water as a phase transition of vaporization takes place below 200 °C rapidly but the slope of the curves decreases up to 500 °C and the total water content is driven off, whereas curves for 600 and 800 °C shows that the LAMM at 600 and 800 °C have relatively low water contents which is not shown in the graph up to 500 °C. The second phase of curves in figures 2 are the chemical changes occurred from the temperature range of 500 to 700 °C. The loss or conversion of the organic compounds has shown in the range of 500 to 700 °C.

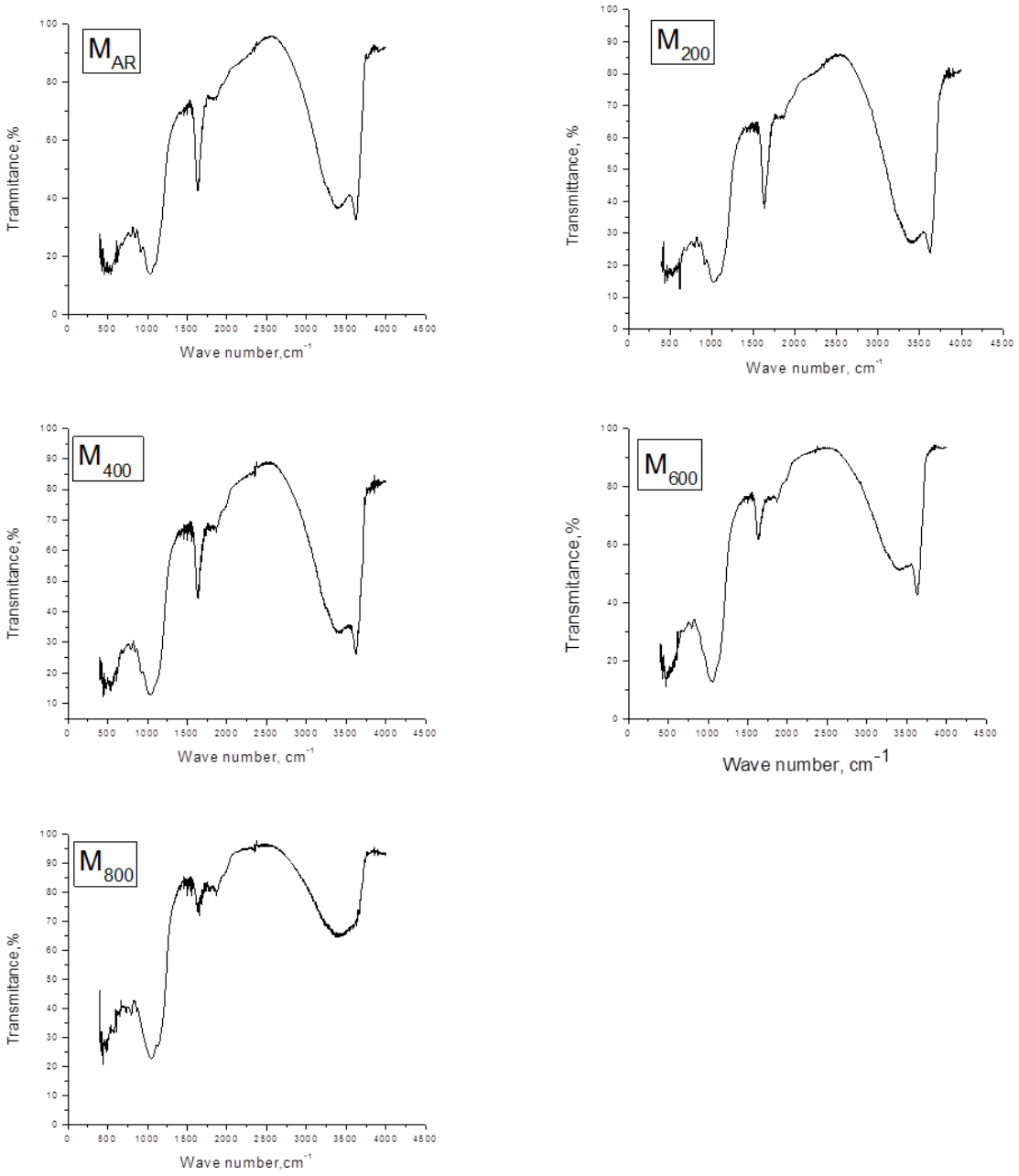

Figure 1: Fourier Transform infrared (FTIR) Spectroscopy of as received and thermally activated samples

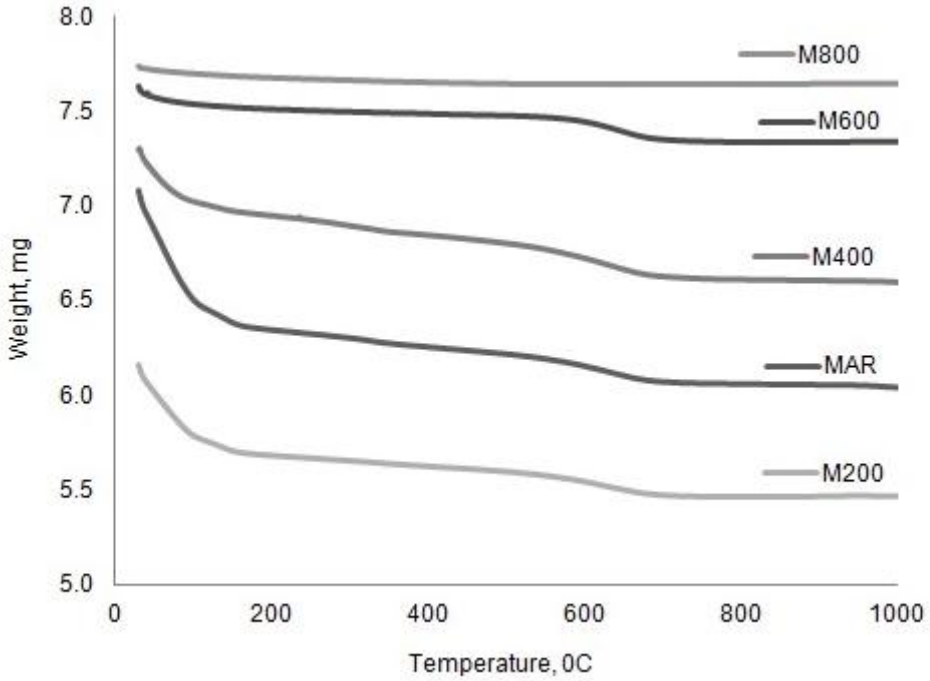

Figure 2: Thermo gravimetric analysis (TGA) of as received and thermally activated samples

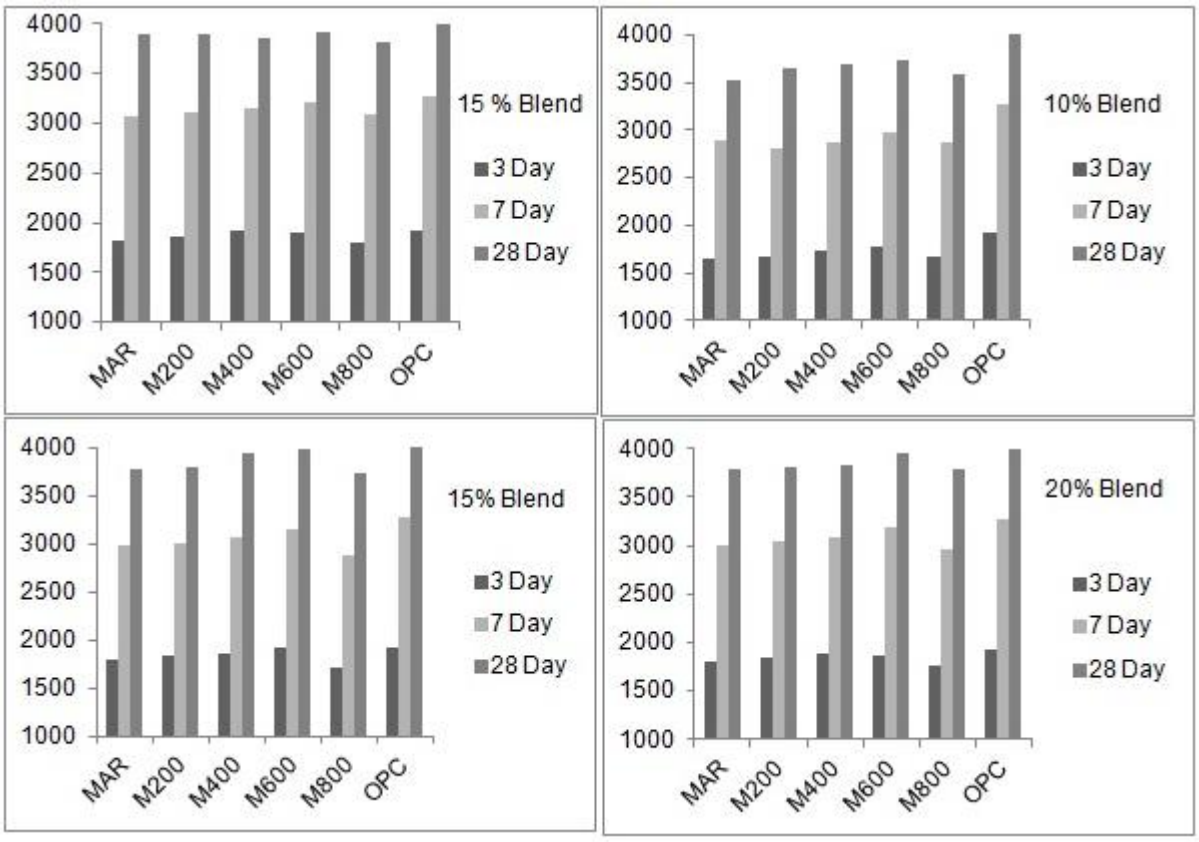

Figure 3: Compressive strength of as received and thermally activated samples

3.4 Mechanical Charecterization

The compressive strength of the as received and thermally activated samples for different blends i.e. 5, 10, 15 and 20 % is shown in Figure 3. The figure shows that as the blend proportion increases, the compressive strength decreases but with the increase in temperature for thermal activation, the compressive strength increases for fixed blend proportions. The early strength, for 3 d are lower which can be attributed to the slow development of pozzolanic reaction but as the time passes the strength gained progressively at the ages of 7 d and 28 d. The initial compressive strength (3 d) of activated LAMM at 600 °C and addition of up to 15 % fulfill the minimum standard of ASTM C150 where as the later age strength of 28 day conformed the maximum compressive strength with the optimum addition of 15 %. The TGA also showed that the free water molecules were evaporated at the temperature up to 280 °C while in the range of temperature from 450 to 580 °C is the region of dehydroxylation and no change was observed after the temperature of 680 °C. Therefore, the thermal activation above this temperature will not make any sense.

3.5 Energy savings and pollution reduction

The results suggest that LAMM can be used as pozzolana up to 15 % by weight if thermally activated at about 600 °C. Replacement of 15 % clinker with mineral material as pozzolana reduces the same amount of raw material from clinkerization process, therefore, by simple logic, reduces energy requirement for size reduction of raw material by 15 % and similarly the thermal energy consumption for clinkerizaion and reduction in the CO_2 emissions.

4. Conclusions

The present study showed that the locally available mineral material found in khybar pakhtunkhwa Pakistan has great potential to act as a pozzolana when treated up to 600 °C. The material was proved to be aluminosilicate as clear from FTIR spectra having reasonable amount of iron content as investigated from XRF study. TGA confirmed that above 600 °C, no change occurred, which may be the optimum activation temperature. Maximum Strength has been achieved by the addition of 15 % LAMM activated at a temperature of 600 °C reducing the energy consumption and emission of green house gases by the same amount making the process more sustainable and environment friendly.

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