Synthesis of Alkali Activated Cement from Local Clay and Its Characterization

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In the present study low cost alternative for Portland cement has been developed by the chemical activation of high kaolinitic clay with NaOH solution. Different parameters affecting the synthesis of binding material and the development of high compressive strength have been studied and optimized. Different parameters of the developed material have been studied. It has been found out that the mixture cured at 80 °C for 48 h has a compressive strength of 45 MPa (6,527 psi) which is far greater than Portland cement. From the mineralogical and microstructural investigations of hardened material, it has been indicated that formation of new phases like sodium zeolite takes place which is directly proportional to the compressive strength. The newly designed material needs only 80 °C and no CO_2 is evolved at all.

1. Introduction

The present cement production is facing two main problems, which have become burning issues both for cement researchers and cement manufacturers. One of the issues is the production of huge amount of greenhouse gases and second is the high cost of the cement, due to the high prices of the fuel consumption in cement plants (Villa et al., 2010). The cement producers are therefore under increasing pressure to reduce the use of energy and associated greenhouse gas emission. Due to the huge amount of concrete used throughout the world as construction material, about 5% of the global emission is due to the production of cement (Habert et al., 2011). Moreover cement production process needs 1,400 °C which needs huge amount of fuel (Cristelo et al., 2011). Different researchers are struggling to reduce the cost of production and emission of gases in one way or the other.

The incorporation of pozzolanic materials in cement in order to reduce the emission of CO_2 and increase the strength and durability of mortars and concretes has become a subject of interest during the last decades (Amin, 2012). Environmental concerns in cement industry have also been addressed by replacing a portion of cement with pozzolanic materials both in mortars and concretes (Habert et al., 2009) which can solve the two problems to some extent. For this reason different pozzolonic materials such as slag, fly ash or silica fume are being used (Amin et al., 2009).

Geopolymers, are considered as the best alternative for Portland cement with smaller or no environmental impacts (Habert et al., 2011). CO_2 production during the calcination of clay minerals is very small as compared to that of Portland cement. Unlike decarbonation in Portland cement, dehydroxylation occurs during the calcination of clay.

During Geo-polymerization an inorganic polymer formation occurs when a solid aluminosilicate react with a strong alkali which act as an activator (Chindaprasirt et al., 2009). The raw material (aluminosilicates) used are usually metakaolinite, or industrial waste like fly ash and blast furnace slag etc. the produced materials at low temperature as a result of alkali activation may be amorphous or crystalline (Guo et al., 2010). During the mixing and handling of geopolymer, a reaction medium is being provided by the water in the geopolymer mixture. Different types of fillers may also be used to improve the desired properties of geopolymers like compressive strength and porosity etc (Rovnanik, 2010). geopolymerization in comparison to Portland cement is very much environment friendly but still have some environment

drawback. For example the application of silicates solutions which involves the dissolving glass at a high temperature is associated with a substantial production of greenhouse gasses (Habert et al., 2011).

Unlike geopolymers, in alkali activated material, replacement of silicate solution with NaOH and metakaolinite with kaolinite further decrease the environmental impacts of the resulting material. Moreover the energy consumption will further be reduced than that of geopolymer as there is no conversion of kaolinite into metakaolinite. The present study is a step toward the development of a low cost building material producing no greenhouse gases and no thermal treatment is required. The main goal is to develop and characterize the high strength alkali activated cementing material by the alkali activation of clay containing kaolinite found in Khyber pakhtoonkhwa Pakistan.

2. Experimental procedure

Kaolinite clay was collected from different areas of Khyber pakhtoon khwa used as a source of aluminusilicate. The chemical composition of clay is given in table 1. NaOH (Merck) was purchased from local market with 99 % purity to prepare the alkali solution using distilled water. Silica sand was also used with clay. The chemical composition of silica sand is given in table 1. Samples were prepared in three steps:

Mixing: clay and silica sand were mixed using a laboratory blender. Alkali solution was prepared with distilled water and stored in plastic bottle to avoid evaporation. To the mixture of clay and silica sand, NaOH solution was gradually added and slurred for 10 min at 200 rpm to make a homogeneous mixture.

Moulding: the paste was moulded in a steel cylinder mould (50x25 mm) and compacted with a pressure of 16 MPa by using a hydraulic compressor. The sample was then de-moulded and weighed. Three specimens were prepared with each mixture.

Curing: the moulded samples were cured in a ventilated oven at 80 °C for 24 h, unless specified otherwise. The compressive strength of the samples was measured by using a compressive strength test machine where the load was applied and increased by a displacement rate of 3 mm/min.

Table 1. Elemental Composition of local Clay and Silica Sand

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K2O	LOI
Clay	58.4	28.7	2.8	0.28	0.3	0.2	0.2	11.33
Silica sand	98.56	0.34	BDL	0.22	BDL	0.11	BDL	0.21

2.1 Mix ratio optimization

Two series of samples were prepared with different ratios of NaOH and Silica Sand to find out the optimal component ratio. In the first series variable amount of NaOH was used i.e. 6-22 %w/w of the total material while in the second series the amount of sand was varied from 0 % to 80 %. Quantity of de-ionized water was taken as the plasticity limit for the mixture of clay and silica sand due to which, the mixture does not flow and is compressed. Other components in mixture were optimized on the basis of compressive strength.

2.2 Optimization of curing conditions

Curing time: The effect of curing time on compressive strength was studied. For this purpose cubes were cured at 80 °C for different times i.e. 6, 12, 18, 24, 48 and 72 h.

Curing temperature: Samples were cured for 24 h at six different temperatures i.e. 40, 50, 60, 70, 80 and 90°C to check the influence of temperature strength development.

Two types of specimens were prepared and cured at optimum conditions. One type of specimens was prepared with Silica Sand filler and the other without sand filler in order to study the influence of sand on the compressive strength.

In order to study the effects of curing conditions on the compressive strength some specimens were cured under laboratory conditions and some were immersed in salt free water. Compressive strength of all specimens was measured after 72 hours. For accuracy three similar samples were tested and the average of the three measurements was taken.

2.3 Characterization of the raw materials and optimized material.

X-Ray fluorescence spectroscopy (XRF) was used to study the elemental composition. Thermo-gravimetry was used to study the thermal behaviour of clay. The heating rate was kept 20 °C/min, starting from 50 °C up to a maximum temperature of 1,000 °C using N_2 atmosphere.

3. Results and discussion

3.1 Characterization of the raw material:

The chemical composition silica sand and clay is expressed in Table 1. It is clear from the table the major components of clay are Silica (SiO_2) and alumina (Al_2O_3) representing more than 70 %. The sand used contains up to 98 % SiO_2 of the total content showing the highest purity. The DTA curve of the clay is shown in figure 1. three endothermic peaks can be seen in the figure at 100, 565 and 970 °C: the first peak corresponds to the dehydration and the second peak which appears at about 565 °C is attributed to the dehydroxylation of kaolinite i.e. removal of hydroxyl groups from Al\OH bonds (Temuujin et al., 2009). The last endothermic peak appears at about 970 °C which corresponds to the formation of new and more stable phases which is a mixture of amorphous materials like mullite and metakaolinite (Zuhua et al., 2009).
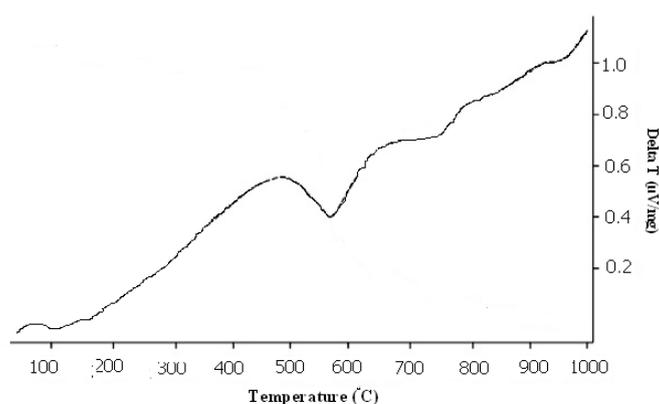
Figure 1: DTA curve of kaolinite clay sample

3.2 Optimization of mixing ratios

Alkali activation is far better than thermal treatment for the aluminosilicate material. The concentration hydroxyl group (OH^-) in the activator is the important parameter. For the disintegration of strong alumino silicate layer strong alkaline medium in highly required. (Sathia et al., 2008). Sodium ion (Na^+) acts as the balancing ion for the negative charge produced by each AlO_4 in tetrahedron.

The effect of alkali content on compressive strength of blended mortars is shown in Figure 2. From the figure it is clear that the strength increases linearly with the concentration of NaOH. The strength increases with the increase in NaOH content reaching upto 33 MPa, but again decreases with further increase of NaOH. The optimum amount of base was found to 16 parts by mass. For further study 16 parts of the base was used.

The sand used in this work is acting as a filler material having a number of positive impacts like reduction of cracking and porosity of the composite. In addition filler material is also acting to reduce the quantity of binder paste making the resultant material less expensive. The impact of sand addition on the compressive strength is shown in Figure 3. It can be seen from the figure that the workability of the binding mixture increases with the increase of sand content. The best compressive strength values are observed for sand to clay ratio of 1 to 1.
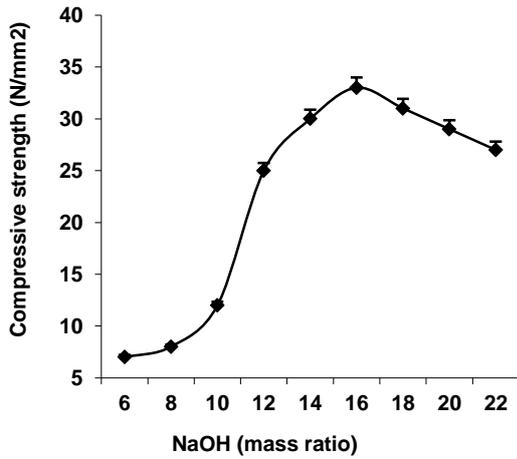
Figure 2: Effect of alkali content on compressive strength of blended mortars
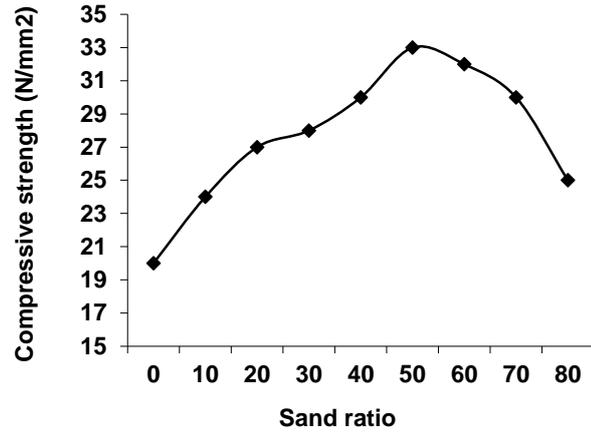
Figure 3: Impact of sand addition on the compressive strength

3.3 Optimization of curing conditions

The relationship of curing temperature with compressive strength is given in Figure 4. The highest compressive strength value was observed at 80 °C of curing. The increase in compressive strength with the increase in curing temperature is due to the increase in reaction rate. Compressive strength also increases with increase in curing time which is shown in Figure 5. The highest strength of 45 MPa was observed for the mixes cured at 80 °C for 48 h. No further improvement in the strength was observed after 48 h showing it as the optimum curing time.

In order to study the effect of moist conditions on the mixes, some samples were kept under wet conditions keeping all other parameters the same. It was observed that samples kept under wet conditions have lower compressive strength than those kept under dry conditions. For this purpose samples were cured tested under dry and wet conditions at room temperature for seven days after curing at 80 °C for 24 h. The average strength of the samples with Silica Sand was 24 MPa in wet and 45 MPa in dry conditions. This indicates that strength increases with curing the mixes in dry condition. The decrease in strength in wet condition is attributed to the absorption of water by the unreacted kaolinite (Cristelo et al., 2011), as well as the hydrolysis of the Si-O-Si bonds in the mixes.
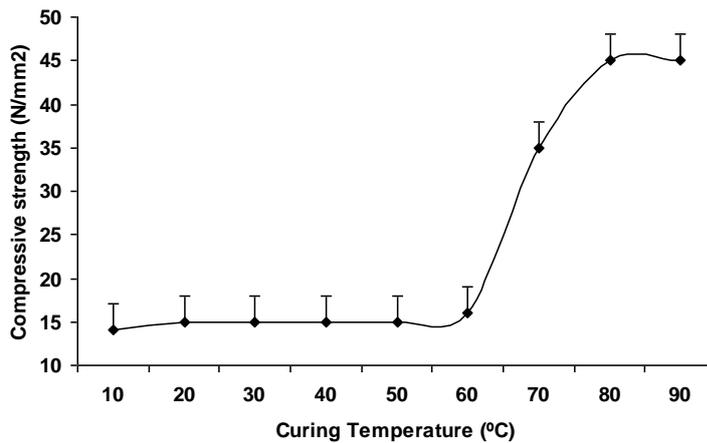
Figure 4: Effect of curing temperature on compressive strength
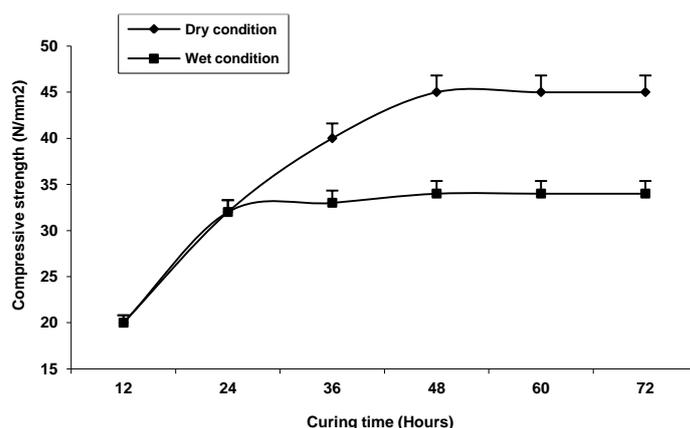
Figure 5: Effect of curing time on compressive strength

3.4 Structural characterization of the optimized material

The DTA curve of the optimized sample is shown in Figure. 6. The first endothermic peak appears in the range of 90-350 °C which is due to the loss of water. The second endothermic peak appear at about 700 °C which may be due to the conversion of kaolinite to meta-kaolinite. This indicates that there is some unreacted kaolinite in the material which is dehydroxilated above 700 °C. A rough quantitative estimation of the unrreacted kalointe is possible from the mass loss (Reddy and Kumar, 2009) but the accurate measurement is not possible due to the formation of new phases at this temperature which overlaps the peak at this temperature range. The third endothermic peak appears at about 970 °C. This may corresponds to the conversion of metakaolinite into comparatively more stable phases, and the decomposition of different sulfates and carbonates present in the clay (Rocha and Klinowski, 1990).
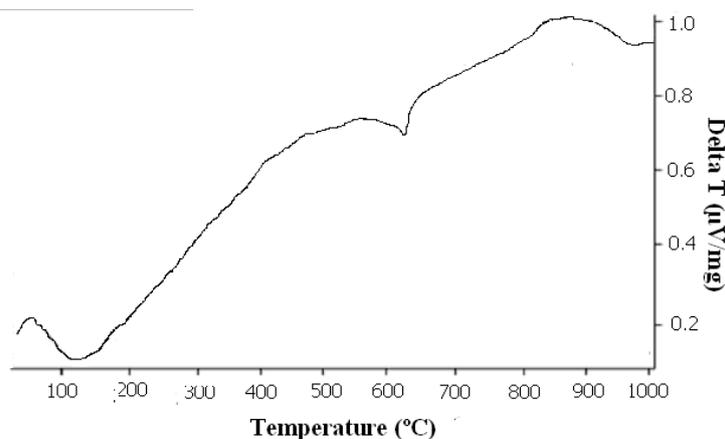
Figure 6: DTA curve of mix formed under optimized conditions

4. Conclusions

The local clay found in khyber pakhtoon khwa Pakistan mainly contains kaolinite and quartz. The clay containing kaolinite was chemically activated with sodium hydroxide solution and characterized using different analytical techniques. The proportioning ratios of different components of mixes was optimized and characterized. The compressive strength of resulting samples was studied under the influence of different parameters like curing temperature, curing time and moisture conditions. The highest compressive strength (45 MPa) of the alkali activated cement was found with clay to sand ratio of 1:1, formed with NaOH and cured at 80 ºC for 48 hours in dry atmosphere. The results showed that unreacted kaolinite was still present which should be decreased to the minimum possible extent and a further increase in the compressive strength is expected. The reaction products of clay and sand in the presence of sodium hydroxide may be sodium aluminosilicate phases from the zeolitic group, which fill the pore spaces and bind the matrix.

1560

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