Conceptualizing Alkali Pozzolan Cement

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Abstract

This paper presents an overview of past research related to the activation of pozzolanic materials and past research related to preparation of alkali pozzolan mortar and concrete by mixing pozzolanic materials and alkali liquids. This research is different from those research, as the aim of this research is not to make mortar or concrete, but to make a 'cement' that could be stored as a product. It investigates the feasibility of producing 'Alkali Pozzolana Cement' (APC) by mixing pozzolanic materials and non-hostile dry form of alkali materials and chemical activators. The main alkali material considered is a dry powder form of lime, and the pozzolanic material used is fly ash. A series of experiments has been conducted, and the initial findings indicate that APC mortar exhibits relatively low strength when compared with OPC mortar. This is due to the slow reaction between alkali and pozzolanic materials and the slow strength gain of the lime-fly ash compound. This has led to a further investigation on the possibility of adding non-hostile activating chemicals to activate the reaction between fly ash and lime and adding small quantity of OPC to enhance the initial strength. Based on the chemical composition of fly ash available in Western Australia, this study proposes the proportion of fly ash and lime to be mixed and the quantity of activating chemicals and OPC to be added. Finally the paper discusses the potential and limitations of APC mixtures and the feasibility of using APC as sustainable cement for the future.

Key words: Alkali Pozzolana Cement, activating chemicals, sustainable cement

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1. Introduction

Numerous researches related to the use of pozzolanic material in preparation of mortar and concrete have been conducted over the years. Certain researches investigate the possibility of replacing Ordinary Portland Cement (OPC) partially by pozzolanic material in preparing blended cements. The other researches investigate the possibility of activating pozzolanic materials by alkali materials in order to prepare mortar or concrete.

Meyer (2009) discusses the recent developments of the use of complementary materials such as fly ash, ground granulated blast furnace slag, silica fume, etc. in preparing concrete. McCarthy et al (2005), based on his experiments, concluded that OPC can be replaced by fly ash up to about 45% by mass to prepare practical concrete. The experimental studies of Oner and Akyur (2007) on the optimum usage of ground granulated blast-furnace slag indicate that the optimum slag percentage is around 55%. Abu Bakar et el (2010) had used 'rice husk ash' as complementary material to substitute OPC by 10% to 40% in order to determine the optimum concrete mix. Partial replacement of OPC by 30% of sugar cane bagasse ash in preparing concrete has been investigated by Paya et al (2000). All these researches are related to partial replacement of OPC by pozzolanic materials.

In the researches related to the activation of pozzolanic materials, different pozzolanic materials and different activating materials had been used. In preparation of geopolymer concrete, fly ash is being activated by sodium hydroxide and sodium silicate (Rangan, 2009). Allahverdi and Ghorbani (2006) used Na_2SO_4, $CaCl_2$, Na_2CO_3, NaCl, and OPC to activate mixtures of natural pozzolan and hydrated lime. Shi and Day (2000b) investigated the effect of Na_2SO_4 and $CaCl_2$ in activating the mixture of natural pozzolan and $Ca(OH)_2$. To activate fly ash, Fan et al. (1999) used Na_2SiO_3, while Katz (1998) used NaOH. Solutions made with NaOH and KOH were used by Palomo et al. (1999).

In most of the above mentioned researches, pozzolanic materials are mixed with different types of alkali liquids to prepare mortar or concrete. Further, when pozzolanic materials are mixed with alkali liquids, chemical reaction starts immediately. Hence those mixtures cannot be stored in a non-reacting dry state. In this background this research investigates the possibility of developing 'new cement' by mixing pozzolanic materials and alkali materials that can be stored in a non-reacting dry state in air-tight bags. In the context of this research, a common name 'Alkali Pozzolana Cement' is given to all the cementitious mixtures of alkali materials and pozzolanic materials. APC is the acronym given to 'Alkali Pozzolana Cement'.

To produce practical cement that can be stored in dry form, and to use at the site, two conditions have to be satisfied. The first condition is that the mixture should not contain any hostile materials, and the second condition is the chemical reaction between materials should not start until water is added.

Islam et al. (2010) describes the mechanism of transforming non-cementitious fly ash into a cementing compound in an OPC-based environment as follows. OPC reacts with water and forms the cementing compound, the chemical name of which is 'Calcium Silicate Hydrate' (CSH). At the same time calcium oxide in OPC is transformed in to Calcium Hydroxide. When fly ash is mixed with OPC, during the hydration process, the Calcium Hydroxide in the OPC paste reacts with fly ash and form Calcium Silicate Hydrate, which is the same cementing compound produced by OPC. The above mechanism is illustrated in Fig. 1.

OPC + **Water** → **Calcium Silicate Hydrate** + **Calcium Hydroxide**

OPC-Fly Ash Mix + Water → **Calcium Hydroxide** (from OPC)+**Fly Ash** → **Calcium Silicate Hydrate**

Fig. 1: Transformation of fly ash into CSH in an OPC-based nnvironment

It is the above mentioned mechanism of transforming fly ash into a cementing compound that created the platform for this research. Accordingly the main aim of this research is to investigate the feasibility of producing new cement by mixing fly ash with calcium oxide and other necessary ingredients.

As a starting point, mixture of fly ash and quick lime (calcium oxide) is considered. When water is added to this mixture, calcium oxide reacts with water and forms Calcium Hydroxide. In this alkali environment, non-cementitious fly ash is transformed into a cementitious compound. The mechanism is illustrated in Fig. 2.

Quick Lime (Calcium Oxide) **+ Water → Calcium Hydroxide**

Quick Lime +Fly Ash + Water → Calcium Hydroxide + Fly Ash → Calcium Silicate Hydrate

Fig. 2: Transformation of fly ash into CSH in an APC-based Environment

Accordingly, in this research, it is expected to use dry powder form of burnt limestone (quick lime) and fly ash to produce APC.

2. Objectives, Methodologies and the Scope of the Research

The main aim of this research is to investigate the possibility of producing 'new cement', called APC, by mixing alkali materials and pozzolanic materials that can be stored in a non-reacting state in air-tight bags. Accordingly the objectives can be describes as follows:

1. To present an overview of Alkali Pozzolan Cement (APC).
2. To investigate different strategies of enhancing early strength of APC mixtures by adding commercially available building materials.
3. To conceptualise APC based on the results of the experiments.

To achieve objectives 1 and 2 experimental methods were used. Experiments were designed to determine early compressive strengths of mortar prepared from selected APC mixtures.

To achieve objective 3, methods of analysis as well as method of synthesis were used. Here the results of the experiments and research findings of available literature were analyzed and then synthesized in order to conceptualize APC mixture.

Scope of the preliminary stage of this research is limited to conceptualization of APC. Accordingly it is expected to conceptually investigate the constituent materials of APC. In the next stage the optimum proportions of constituent materials of APC will be determined.

3. Experimental Program, Results and Analysis

As different types of APC mixtures were prepared by mixing fly ash and quicklime in different proportions, it was essential to differentiate the APC mixtures. Hence the following nomenclature was adopted within the context of this research. To indicate the percentage of pozzolanic material present in the fly ash – quicklime mixture, a two digit number is used as the suffix of the acronym

APC. Accordingly the common form 'APCnn ' is used to identify a mixture. Where 'APC' stands for 'Alkali Pozzolan Cement' and 'nn' indicate the percentage of pozzolan in alkali-pozzolan mixture, the remainder is quicklime. For example APC mixture that contains 70% of pozzolanic material is named as APC70 (The remaining 30% is lime).

Raw Materials

For all the experiments conducted in the preliminary stage of this research, commercially available fly ash (Class F), quick lime (burnt limestone powder), Ordinary Portland Cement (OPC), gypsum, and sand available in Western Australia were used. Chemical analysis was done to determine the composition of fly ash and quicklime, and the results are shown in Table 1. Sieve analysis results of sand is shown in Table 2.

Material	**% of constituent materials**			
	CaO	**SiO_2**	**Al_2O_3**	**Other**
Fly Ash	1.57	51.56	27.60	19.27
Quick Lime	56.52	2.13	0.50	40.85

Table 1: Chemical composition of fly ash and quicklime.

Sieve	**% Passing**
1.18 mm	99.77
850 µm	96.70
600 µm	77.94
425 µm	47.78
300 µm	25.50
150 µm	2.62

Table 2 : Sieve Analysis Results

In preparing mortar, cement to sand ratio (c/s ratio) was kept as 1: 1 and water to cementitious mixture ratio (w/c ratio) was kept as 0.45. Size of the specimens was 50mm x 50mm x 50 mm. The specimens were cured under ambient conditions and compressive strengths were tested on 7, 14, 21 and 28 days. In determining compressive strength, three specimens were tested and mean values were taken.

Experiment 1

Experiment 1 was designed to get a brief idea about the strength development of APC under ambient curing, as most of the literature available is related to curing at elevated temperatures. Three APC mixtures, namely APC60, APC70, and APC80, were used to prepare mortar specimens. Compressive strengths of mortar are shown in the Table 3.

Cementitious Mixture	**Compressive Strength (MPa)**			
	7 day	**14 day**	**21 day**	**28 day**
APC60	0.6	1.0	1.5	1.8
APC70	0.5	0.7	0.9	1.1
APC80	0.3	0.4	0.5	0.8

Table 3: Compressive strengths of different APC mixtures

Experiment 2

Experiment 2 was designed to investigate the possibility of improving the strength by adding small quantity of gypsum or OPC. APC70 was chosen and different mixtures were prepared by mixing APC70 with gypsum or OPC in different percentages. Compressive strengths of mortar are shown in the Table 4.

Cementitious Mixture	**Compressive Strength (MPa)**			
	7 days	**14 days**	**21 days**	**28 days**
100% APC70	0.5	0.7	0.9	1.1
95%APC70 + 5% Gypsum	0.9	2.5	3.3	3.8
90%APC70 + 10% Gypsum	0.5	2.3	4.4	4.8
80%APC70 + 20% OPC	1.5	3.2	3.3	3.9
70%APC70 + 30% OPC	4.1	6.5	7.1	7.0

Table 4: Effect of addition of Gypsum and OPC on Compressive strength of APC70

Analysis of the results

Results of the experiment 1 exhibit relatively low strengths of APC mortar. This is due to the slow reaction between alkali and pozzolanic materials and the slow strength gain of the lime-fly ash compound. Results of the experiment 2 show that the compressive strengths of mortar can be significantly improved by adding small quantities of gypsum or OPC.

4. Conceptualisation of APC

The main aim of the stage 1 of this research is to conceptualise an APC mixture that can be stored and used under non-laboratory conditions to prepare mortar and/or concrete practically.
To conceptualise constituent materials of APC, the findings of the experiments and the findings of the available literature were used.

The results of the experiments show that strength gain of the APC mortar is very low. This may be due to slow formation of calcium silicate hydrate and slow strength gain of calcium silicate hydrate.

Li et al. (2000) states that fly ash can be activated by breaking down the glass phases of fly ash particles. For that purpose an alkali environment of pH value 13.3 or higher is required. The APC mixture considered in this research consists of fly ash and calcium oxide. When water is added, calcium oxide in the mixture transforms in to calcium hydroxide. However, the pH value of fly ash-calcium hydroxide environment is less than 13. Hence, fly ash cannot be activated solely by calcium hydroxide.

Normally to achieve an environment of pH value over 13, strong alkalis are added. Common method of activating fly ash is by mixing with NaOH solution. However, NaOH is a hazardous and hostile chemical. Further as soon as fly ash is mixed with NaOH solution, the chemical reaction starts. This hinders the use of NaOH in producing pozzolanic cement that can be stored in dry form and in a non-reacting state to be used under non-laboratory conditions safely.

Shi and Day (2000) investigated the effect of adding small quantities of Na_2SO_4 to increase the alkalinity in order to activate natural pozzolan-$Ca(OH)_2$ mixture. The relevant chemical reaction is given below.

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH$$

If a small quantity of Na_2SO_4 is added, only a small quantity of NaOH will be formed. Further it is formed within pozzolan- $Ca(OH)_2$ mixture. Hence it would not behave as a hostile compound. Hence Na_2SO_4 has been identified as a chemical that can be used to increase alkalinity in APC mixture.

When water is added to the mixture of APC and Na_2SO_4 , first, quicklime (CaO) will be transformed in to $Ca(OH)_2$. In the presence of additional water, $Ca(OH)_2$ reacts with Na_2SO_4 and forms NaOH as described above. Formation of NaOH, increases the alkalinity of the environment, and in that environment glass phases of fly ash particles will be broken and provide opportunity to react with $Ca(OH)_2$ to produce Calcium Silicate Hydrate.

Although adding Na_2SO_4 would activate fly ash-quicklime mixture, still it will take longer time for mortar to gain strength; hence early strength will be low. In order to improve early strength of mortar some quantity of OPC is added to the mixture.

Finally the APC can be conceptualised as a mixture of fly ash, quicklime and small quantities of Na_2SO_4 and OPC. Scope of the preliminary stage of the research is limited to conceptualization of APC and it has been achieved. In the next stage of the research, optimum proportions of the constituent materials have to be determined. In conceptualising APC, and improving its properties, the method used by Helmuth (1987) is adopted, and it is outlined below.

SiO_2 in fly ash reacts with CaO and water; and forms 'calcium silicate hydrate'. It is assumed that, after complete reaction, the average CaO to SiO_2 molar ratio in calcium silicate hydrate is 1.0. The equivalent CaO to SiO_2 weight ratio is 0.93. In addition, Al_2O_3 in fly ash reacts with CaO and water; and forms 'gehlenite hydrate'. Gehlenite hydrate has CaO to SiO_2 plus Al_2O_3 molar ratio of 1.0. The equivalent weight ratio is 0.55.

According to the chemical analysis, fly ash used in the experiments of this research contains 51.5% of SiO_2 and 27.6% of Al_2O_3. The percentage of CaO is 1.5% and hence can be neglected. Accordingly, the quantity of CaO required for complete reaction with fly ash can be calculated as below.

Quantity of CaO = 0.93x51.5% + 0.55x27.6% = 0.630 kg of CaO per 1 kg of fly ash
Or
1.59 kg of fly ash per 1kg of CaO = 1.20 kg of fly ash per 1 kg of $Ca(OH)_2$

At complete hydration, 1 kg of cement releases about 0.24 kg of $Ca(OH)_2$. It has already been determined that 1.0 kg of $Ca(OH)_2$ reacts with 1.20 kg of fly ash. Hence 0.24 kg of $Ca(OH)_2$ reacts with 1.2x0.24 kg (=0.29 kg) of fly ash. Hence quantity of hydrated lime released by 1 kg of cement is adequate to react with 0.29 kg of fly ash.

According to the chemical analysis, the quicklime used in the experiments of this research contains 56.5% of CaO.

Consider 100 grams of fly ash-quicklime mixture. Assume that the mixture contains p grams of fly ash and (100-p) grams of quicklime. Then the CaO in the mixture is 0.565(100-p) grams. According to above calculations, 1 kg of CaO reacts with 1.59 kg of fly ash. Hence 0.565(100-p) grams of CaO would react with 1.59x0.565(100-p) grams of fly ash. Then the remaining quantity of fly ash will be equal to [p -1.59x0.565(100-p)] grams. The quantity of OPC needed to react with the remaining fly ash is {[p -1.59x0.565(100-p)]/0.29 } grams of cement.

By varying the value of p, a spectrum of APC can be determined. The strength of the final mixture will depend on the quantity of Na_2SO_4 added to activate fly ash, and also on the quantity of OPC added. If p = 55 is selected, the quantity of fly ash and quicklime are 55 grams and 45 grams respectively. This mixture is named as APC55. Then the quantity of OPC needed to react completely with the excess fly ash in APC55 can be calculated using the above formula, which is, 100 g of APC55 is to be mixed with 50.25 g of OPC. To activate fly ash, small quantity of Na_2SO_4 is also added. Accordingly the final mixture can be specified as: 63% of APC55 + 32% of OPC + 5% of Na_2SO_4 (where APC55 is a mixture consisting of 55% of fly ash and 45% of quicklime).

5. Conclusion

The main objective of this research is to investigate the possibility of producing cement (APC) that can be stored in dry non-reacting state. To achieve this objective, fly ash and quick lime were used as main raw materials. Fly ash and quicklime were mixed according to three different proportions to prepare mortar specimens and their compressive strengths were determined. The results of the experiment 1 showed that the early compressive strengths were relatively low. However the results of the experiment 2 showed that the strengths can be significantly improved by adding a small quantity of gypsum or OPC. This information has led to theoretically investigate the possibility of improving the strength of APC mortar by adding non-hostile activating chemicals and OPC to enhance initial strength. Accordingly the cementitious mixture has been conceptualised as a mixture of fly ash, quicklime and small quantities of Na_2SO_4 and OPC. From the mixtures used in experiment 2, the mortar strength could achieve 7 MPa in 28 days, which means that a higher strength can be achieved by the conceptualised mixture. At this state of the research, the proposed mix of APC can be used in preparing mortar, producing cement bricks, or used for non-structural applications such as foot-path and lean concrete for foundations, etc. If APC can be used, even with limited applications, the use of OPC can be reduced. Further the main raw material used in producing APC is fly ash, which is a by product of coal power stations. Fly ash is usually sent to dumping field and contributes to land pollution. Hence utilizing fly ash will also help reduce land pollution. Therefore, if successfully developed, APC can be considered as sustainable cement for the future.

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