

Chemical Activation of Low Calcium Fly Ash

Part 1: Identification of Suitable Activators and their Dosage

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INTRODUCTION

Fly ash is a pozzolanic material widely used as a mineral admixture. In the case of a highly reactive ash it may replace 20 to 30% of the cement¹. Low calcium fly ash as a cementitious material has an inherent drawback - its relatively low reactivity. Thus an external agent is required to accelerate the hydration reactions. Though the use of alkaline activators to stimulate the latent pozzolanic properties dates back to history², the research on alkali activators in fly ashes is relatively new. The intrinsic reactivity of a fly ash depends upon various factors, primarily its chemical and mineralogical composition and fineness³⁻⁵. In an aqueous system, hydroxyl ions (OH)⁻ are known to increase the reaction rate by promoting the dissolution of the aluminate and silicate network⁶. The hydroxyl ions maybe introduced from strong alkalis such as NaOH or aqueous silicates with low SiO₂/Na₂O modulus, or from weak alkalis such as Na₂CO₃, Ca(OH)₂, or silicate with high SiO₂/Na₂O modulus⁷. The main objective of this work is to identify a combined chemical and mechanical activation system by which highly reactive fly ash suspension can be prepared. A wide variety of inorganic salts have been used in this study. These formulations have been used with both coarse and fine varieties of fly ash to determine their influence.

EXPERIMENTAL

Low calcium fly ash (PSU-MRL code: B 97) and Ordinary Portland Cement (PSU-MRL code: I 40, ASTM Type I) were used for preparing OPC: fly ash cement pastes. The chemical compositions of these materials are given in Table 1. The main chemical activators investigated included: hydroxides of calcium and sodium in various concentrations, sodium carbonate, sodium sulfate, sodium chloride, nitrates of sodium, ammonium and calcium and binary mixtures of some of these compounds. The various inorganic salts used in this study were either AR/GR or Reagent Grade chemicals.

1. Fineness

The as received fly ash was coarse in nature. The BET measurement of the as received ash showed a surface area of 1.16 m²/g. Grinding of the coarse fly ash was carried out in an attrition mill using zirconia balls in an ethanol medium. The following ratio of ash: ethanol: grinding media was used in the attrition mill: 150 g coarse ash: 300 ml ethanol: 1000 g Zirconia balls.

Surface area measurements of the different fractions collected were carried out using the Monosorb Surface Area Analyzer, Model MS-12, supplied by Quantachrome. The particle size distributions of selected fractions of the ash were determined by a Sedigraph instrument supplied by Micromeritics. Table 2 gives the comparative particle size distribution of coarse and milled ash at different grinding duration. The maximum gain in fineness was obtained within 10 minutes of grinding. Based on this study, coarse ash attrition milled for 10 minutes was taken for studies.

2. Preparation of Reactive Fly Ash Suspension

A novel method was used for the preparation of chemically activated fly ash suspension. A forty-gram portion of the ash was dispersed in 60 grams of de-ionized water in a 500 ml glass beaker. The various activators (inorganic salts) were added to the slurry in different concentrations. The contents were covered with a watch glass and digested with magnetic stirring for 2 hours at 90 °C using a hot plate. The contents were cooled and the water lost during the digestion was replaced. The treated ashes were blended with OPC in the slurry form to make cement paste.

3. Cement - Fly Ash Paste Preparation

Ordinary Portland Cement (OPC), and OPC and untreated and treated coarse and fine fly ashes were mixed in the ratio of 80:20. The water content was maintained at the ratio of W/S= 0.30 for all the studies. When used in the slurry form, the liquid phase was the same solution as used during the chemical treatment of the ashes.

4. Compressive Strength Measurement

Compressive strengths were measured on 25mm x 25mm x 25mm cubes. Paste samples were mixed using modified American Petroleum Institute (API) procedure and cast into the cubes. After one day of curing, the molds were removed. The specimens were cured in a 25 °C curing chamber for 1-day, and in a 38°C curing chamber for 27 days. The specimens were cured in a closed container over water. The compressive strengths of 3 samples each were measured after 1 and 28 days. The compressive strengths were measured using a Tinius Olsen instrument supplied by Testing Machine Company, Willow Grove, PA, and USA. The crosshead speed was maintained at 0.05” /minute for all the measurements. The hydrated samples of the hydrates were freeze dried and stored for further characterization.

RESULTS

A systematic study was carried out to identify the most appropriate activators that will enhance the reactivity of the low calcium fly ash at the early stages of curing. Various activators, in single and in binary/ternary combinations, with varying concentrations were used for the chemical activation. For the studies under consideration here, the prepared suspensions were used in the slurry form. In the second series, the combined effect of mechanical and chemical activation was studied using the 10 minutes milled fine ashes. Results of compressive strengths obtained for the ashes treated with various activators are given in Table 3. These results were compared with compressive strengths of the control mixtures (Figure 1). The compressive strengths reported here are for 1 and 28-day hydration.

The 0.08 N NaOH activated sample had both 1-day and 28-day strengths higher than the 80:20 OPC:Ash control mixture and 28-day strength higher than 100% OPC control mixtures. The samples activated by high concentrations of sodium hydroxide (0.8 N), show lower 1 and 28-day strengths than the 80:20 control mixture. Binary mixtures of calcium and sodium hydroxides at high concentration produced low strength 1 and 28-day. Single and binary salts of sodium carbonate showed a very poor activation at 1-day hydration. The calcium nitrate ($\text{Ca}(\text{NO}_3)_2$ 1.666N) activated specimens showed a lower 1-day strength and higher 28-day strength than the 80:20 control mixture. Nitrates of ammonium and sodium activated samples produced roughly equal 1-day strength and higher 28-day strength than the 80:20 control mixture. Calcium chloride and calcium nitrate activated samples produced lower early strength and equal 28-day strength.

Combined effect of mechanical and chemical activation was studied using the ground ash. The chemical components used in this study were a) sodium hydroxide in low concentration (0.08 N), b) binary mixture of calcium hydroxide and sodium sulfate and c) ternary mixture of sodium carbonate, calcium hydroxide, and sodium sulfate. The 1 and 28-day compressive strengths obtained for these samples are given in Figure 2 and 3 respectively. All the formulations produced higher 1 and 28-day strengths than the respective coarse ash. They also produced higher compressive strength than the control mixtures (Figure 1). Among the activators used, sodium hydroxide in low concentration (0.08 N) produced higher compressive strength than the binary and ternary activators.

DISCUSSION

According to Table 3, about half of the treated samples improved their 1-day strength and nearly all the formulations produced higher 28-day strengths than the untreated fly ash. On the other hand when compared to 100 OPC control mixture, all the formulations produced lower 1-day strength. Ashes treated with low concentrations of alkali salts produced higher 28-day strength than the 100% OPC control mixtures, but the compressive strength decreased for the ashes treated with higher concentrations of activators. Studies indicate that there is no definite correlation between the compressive strengths obtained and the pH of the treated suspensions. The reactivity of the fly ash increases after wet processing with the chemical activators at low concentrations. The wet processing of the fly ash with alkaline activators has created active surface by attacking the soluble silicates at high pH. The increase in reactivity also observed in finely ground fly ash particles. The rheology of the fresh paste dependent on the ash fineness⁸. High strength for the formulations containing the fine ash is partly due to dense packing of very fine ash particles between the larger particles of the portland cement. Grinding, as a physical process cannot change the polarity of O-Si-O and O-Al-O bond, of the glassy phase, but could cause more or less breakage of O-Si-O and O-Al-O bonds. As a result, glass surface no longer keeps its original stable state; the incomplete coordinated Si^{4+} is likely to be exposed on the particle surface, so that the surface free energy of glass is increased. New active surface is continuously created when the particles of fly ash are repeatedly ground.

CONCLUSION

Sodium carbonate alone show very weak activation effect but a mixture of sodium hydroxide, sodium carbonate, and calcium hydroxide produces improved strength. Binary mixtures of calcium and sodium hydroxides at high concentration produce low 1-day strength. Nitrate salts of calcium, sodium, and ammonium show a low activation effect. Calcium chloride produces lower early strength and equal 28-day strength. The activated fine ash produces better strength than the respective activated coarse ash. Of all the activators studied only the sodium hydroxide in low concentration meets or exceeds the performance of 100 % OPC. Activation effect can be enhanced if mechanical activation is combined with chemical activation.

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Table 1 - Chemical Analysis of the Raw Materials used in the Study.

Oxide (wt %)	OPC (Type-1)	Fly Ash (B 97)
SiO ₂	20.7	48.4
Al ₂ O ₃	5.09	25.9
TiO ₂	0.21	1.31
Fe ₂ O ₃	2.00	16.1
MgO	2.95	0.75
CaO	63.1	1.73
MnO	0.06	0.029
Na ₂ O	0.30	0.24
K ₂ O	0.91	2.19
P ₂ O ₅	<0.05	N.A.
SO ₃	3.20	0.31
L.O.I.	1.92	1.90
Trace Elements	<0.1	<0.1

Table 2. Effect of Grinding Duration on the Particle Size Distribution of Fly Ash

Size (microns)	Cumulative Percent less than		
	Coarse	10 minutes milling	20 minutes milling
50	100	100	100
40	100	100	100
30	95	100	100
20	80	100	100
10	55	85	90
5	20	55	70
1	-	20	55

Table 3. 1 and 28-Day Compressive Strengths obtained for OPC- Ash Admixtures Activated with Various Chemical Salts.

Activator	Compressive Strength (MPa)		Wt % of Activators with respect to Fly Ash
	1-day	28-day	
OPC	58	91	-
OPC + Coarse Ash	43	61	-
OPC + Coarse Ash after water leach	43	73	-
NaOH (0.08 N)	44	99	0.5
NaOH (0.8 N)	37	61	5
0.78 N Ca(OH) ₂ + 0.42 N NaOH	30	66	6.81
0.78 N Ca(OH) ₂ + 0.42 N Na ₂ SO ₄	44	90	13.19
NH ₄ NO ₃ (0.18 N)	41	81	2.2
NaNO ₃ (0.8 N)	45	83	5.31
Ca(NO ₃) ₂ (1.7 N)	28	77	20.5
0.08 N NaOH + 0.16 N Ca(OH) ₂	46	82	1.36
0.08 N NaOH + 0.17 N Na ₂ CO ₃	28	94	1.825
Na ₂ CO ₃ (1.67 N)	17	30	13.25
0.08 N NaOH + 0.17 N Na ₂ SO ₄	31	68	2.275
CaCl ₂ (1.67 N)	37	90	6.95
0.16 N Ca(OH) ₂ + 0.17 N Na ₂ SO ₄	44	75	2.635
Na ₂ CO ₃ + Ca(OH) ₂ + Na ₂ SO ₄ (0.17 N + 0.16 N + 0.17 N each)	49	85	3.96

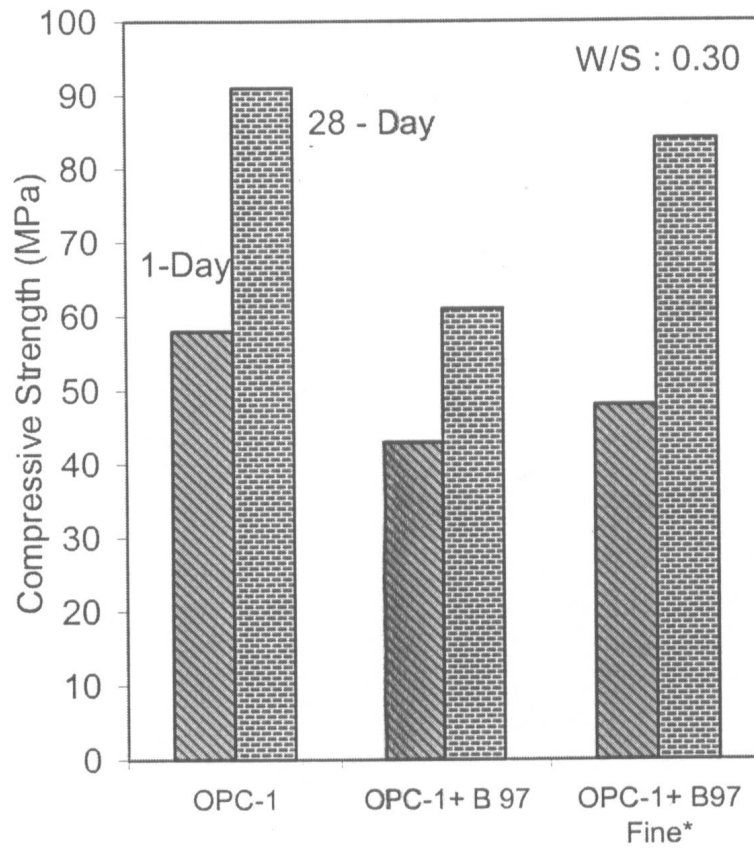


Figure 1. Compressive Strengths Obtained for OPC-Fly Ash Control Mixtures

Figure 2. 1-Day Compressive Strengths obtained for Mechanically and Chemically Activated OPC-Fly Ash Admixtures

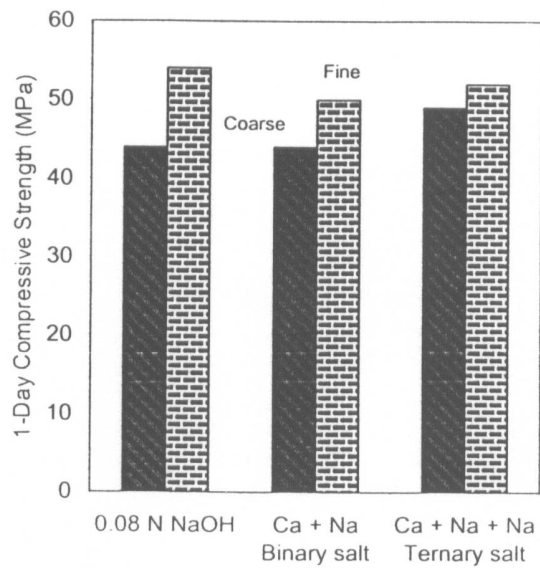


Figure 3. 28-Day Compressive Strengths obtained for Mechanically and Chemically Activated OPC-Fly Ash Admixtures

