

ACTIVE ALKALIS IN CEMENT-FLY ASH PASTE

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1. ABSTRACT

Active alkali content of cement-fly ash pastes was studied by using two types of cements, a type I high-alkali cement and a type II low-alkali cement, and three Class C fly ashes. The concentration of active alkalies was measured using the procedures modified from ASTM C 311 for available alkali test. The purposes of this research were to study: (1) the significance of standard available alkali test for analyzing active alkalies in actual cement-fly ash paste, and (2) the relationship between the active alkali concentration and the chemical compositions of the cement-fly ash paste.

The results indicated that the available alkali test described in ASTM C 311 tends to underestimate the ultimate active alkali content in actual cement-fly ash paste. An empirical equation, % Eq. $\text{Na}_2\text{O} = -0.1486 + 28.6153 (N/S)$, was developed to estimate the ultimate concentration of active alkalies in cement-fly ash paste from the known N/S mole ratio in the reacting system. It was also found that more than 85% of total equivalent alkalies contained in the paste tended to be mobilized into the pore solution when the C/S mole ratio in the paste was greater than 1.75.

2. INTRODUCTION

Addition of fly ash to concrete is frequently used to mitigate the deleterious expansion due to the alkali-aggregate reaction. However, a certain amount of alkalies may be released from the fly ash itself; this enhances the reaction. ASTM C 311 provides a test method to determine the amount of alkalies that will be available from fly ash. The test consists of reacting 5g of fly ash, 2g of calcium hydroxide and 10 ml water for 28 days at 38°C, extracting the available alkalies (Na_2O and K_2O) with water and determining their concentration with flame photometry. The use of fly ash or other pozzolan is governed by ASTM C 618 which specifies that the maximum allowable available alkali content, instead of total alkali content, is 1.5% equivalent Na_2O ($\% \text{Na}_2\text{O} + 0.658 \times \% \text{K}_2\text{O}$). However, it has been found that the rate and amount of extraction of sodium and potassium ions increase as pfa: $\text{Ca}(\text{OH})_2$ mass ratio decreases, and all of the sodium and potassium ions presented in the fly ash would ultimately be extracted if the pfa: $\text{Ca}(\text{OH})_2$ mass ratio is low [1]. The available alkali test tends to underestimate the ultimate amount of alkalies that may be extracted from a fly ash-calcium hydroxide mixture after long periods of curing at 38°C [2].

In this research, active alkali content of cement-fly ash pastes was studied. The term "active alkalis" is defined as the alkalis which can be mobilized from the cement-fly ash paste into the liquid phase during hydration of the paste, and which are supposed to induce the alkali-aggregate reaction. The purposes of this research were to study: (1) the significance of standard available alkali test for analyzing active alkalis in actual cement-fly ash paste, and (2) the relationship between the active alkali concentration and the chemical compositions of the cement-fly ash paste.

3. EXPERIMENTAL

In order to study the active alkali content in actual cement-fly ash paste, two types of cements, a type I high-alkali (DAV) and a type II low-alkali (ND) cements, and three Class C fly ashes with various alkali contents were used. The abbreviations and chemical compositions of cements and fly ashes are given in Table 1. The available alkali contents, measured according to ASTM C 311, of three fly ashes were in the range of 1.46 to 3.42. Only NE4 fly ash met the requirements specified in ASTM C 618 as a mineral admixture in concrete containing reactive aggregate.

Both cements were mixed separately with all three fly ashes for 0, 15, 25 and 40 percent replacements by volume. Five gram samples of cement-fly ash mixture were mixed with 10 ml deionized water and sealed in vials cured at 38°C. Active alkali contents of each paste were extracted with hot water and measured by flame photometry after 28 days and 3 months of curing.

Table 1. Abbreviations chemical compositions of cements and fly ashes

	Cement		Fly Ash		
	DAV	ND	ONT	OTT	NE4
CaO	63.25	64.33	13.10	24.25	27.19
SiO ₂	21.84	22.17	40.70	31.55	33.29
Fe ₂ O ₃	2.48	3.80	4.80	4.90	6.17
Al ₂ O ₃	4.34	4.25	19.10	17.71	15.83
MgO	2.53	1.81	2.70	4.78	5.80
SO ₃	2.27	2.39	1.49	3.18	3.76
TiO ₂	0.25	0.21	0.99	1.35	1.03
P ₂ O ₅	0.12	0.08	0.55	1.81	0.85
Na ₂ O	0.26	0.13	6.92	3.13	2.10
K ₂ O	0.89	0.55	0.69	0.40	0.25
Total Alkalies, % Eq. Na ₂ O	0.85	0.49	7.37	3.39	2.26
Available Alkalies, @ 28 days, % Eq. Na ₂ O	----	----	3.42	2.16	1.46
Specific Gravity	3.15	3.15	2.45	2.63	2.64

4. RESULTS AND DISCUSSION

Active alkalis in cement-fly ash paste can be expressed either as the percent equivalent Na₂O (% eq. Na₂O) by weight of the paste or as the percentage of total equivalent alkalis in the paste. The term "concentration of active alkalis" is used when the active alkali content is expressed as % eq. Na₂O by weight of cement-fly ash paste, and "amount of active alkalis" is used when it is expressed as the percentage of total equivalent alkalis in the paste.

The concentration of active alkalis extracted from cement-fly ash pastes after 28 days and 3 months of curing at 38°C are shown in Figure 1. The measured concentration of active alkalis as well as the total equivalent alkalis in the paste increased proportionally with the percentage of fly ash replacement. The active alkali concentrations increased with time approaching the total alkali concentrations in most of the pastes after 3 months of curing.

The amount of active alkalis released from the cement-fly ash pastes are plotted in Figure 2 as a function of fly ash replacements. When cured for 28 days, the amount of active alkalis steadily decreased with increasing percentage of fly ash replacement due to slow hydration of fly ash as compared with cement hydration. For all cement-fly ash pastes, more than 85% of total equivalent alkalis mobilized into the liquid phase becoming active for alkali-aggregate reaction after 3 months of curing. Thus, the total equivalent alkali content in the pastes with and without Class C fly ash can be conservatively considered as active for alkali-aggregate reaction.

Results obtained from this research and results obtained earlier from the available alkali tests for six Iowa fly ashes [2] are combined to study the mobilization of alkalis from both cement-fly ash pastes and fly ash-calcium hydroxide mixtures prepared according to ASTM C 311. A good linear relationship, shown in Figure 3, exists between the concentration of measured ultimate active alkalis and the N/S mole ratio in the paste. The concentration of active alkalis increases linearly with increasing N/S mole ratio in the paste. This indicates that the concentration of active alkalis in the pore solution depended not only on the total alkali content but also on the silica content of the paste. A linear regression equation,

$$\% \text{ eq. Na}_2\text{O} = -0.1486 + 28.6153 (N/S)$$

was developed to estimate the concentration of active alkalis in cement-fly ash or fly ash-calcium hydroxide paste when the elemental composition in the reacting system is known.

It was also found that the amount of active alkalis, expressed as the percentage of total equivalent alkalis, was dependent on the C/S mole ratio in the reacting system. More than 85% of total equivalent alkalis might be ultimately mobilized to the liquid phase when the C/S mole ratio was greater than 1.75. This indicates that the effectiveness of using fly ash as a mineral admixture in concrete to reduce the risk of deleterious alkali-aggregate reaction is dependent mainly on the total alkali, silica, and calcium contents in the fly ash. Fly ash with higher silica, lower alkali, and lower calcium contents would have better effects on reducing damages caused by alkali-aggregate reaction. Silica fume or Class F fly ash may be recommended

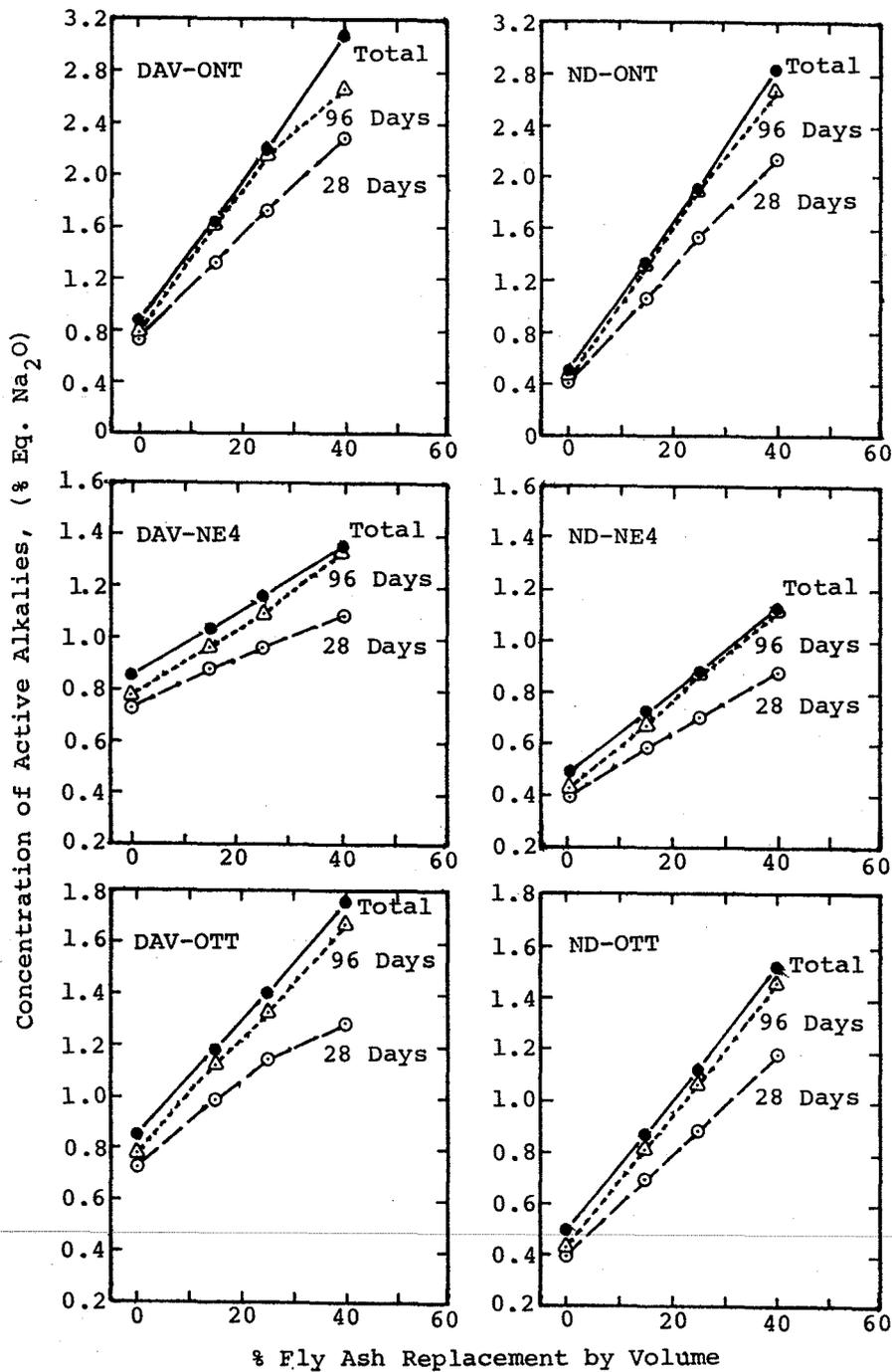


Figure 1. Concentrations of active alkalis for cement-fly ash pastes

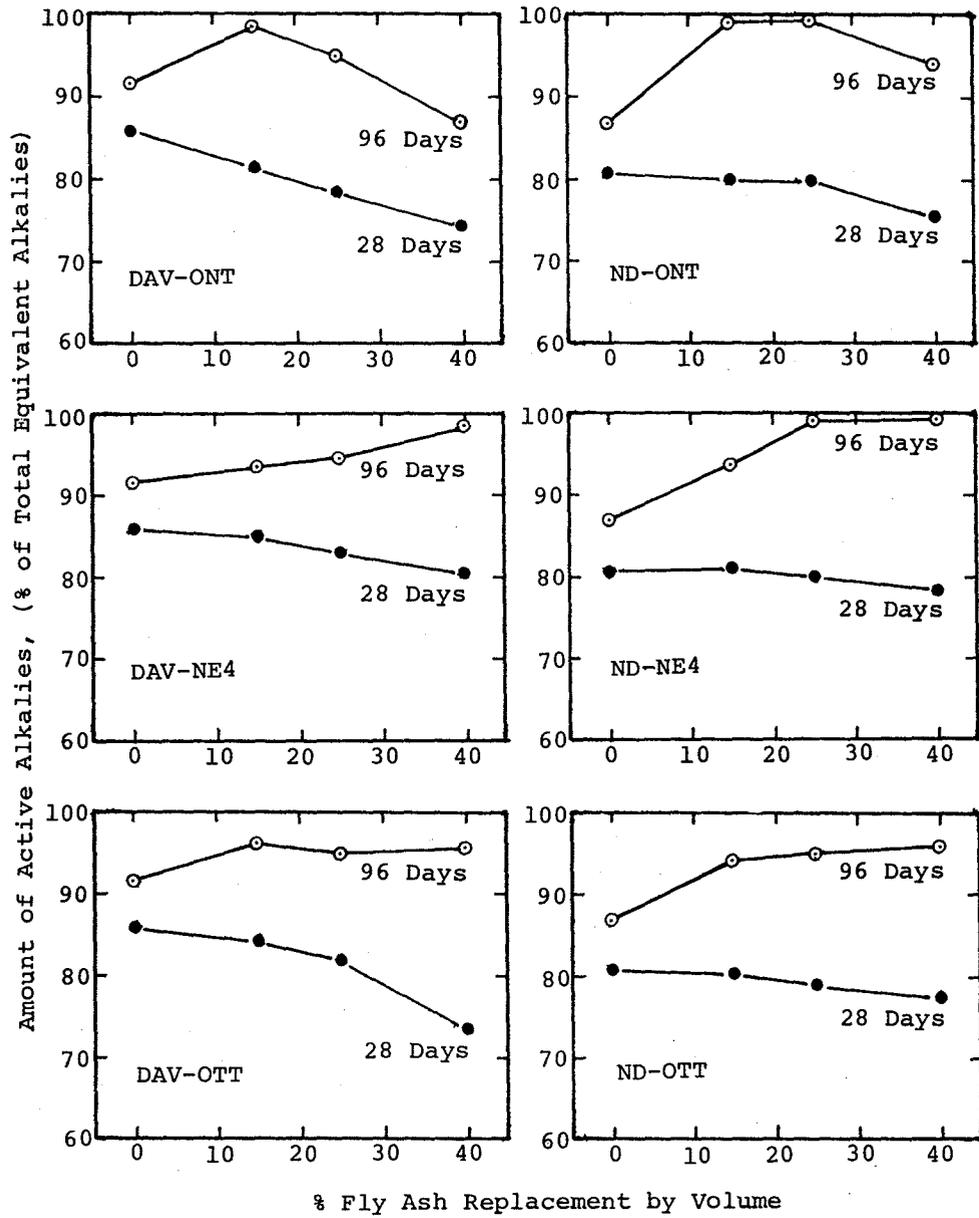


Figure 2. Amount of active alkalis extracted from cement-fly ash pastes

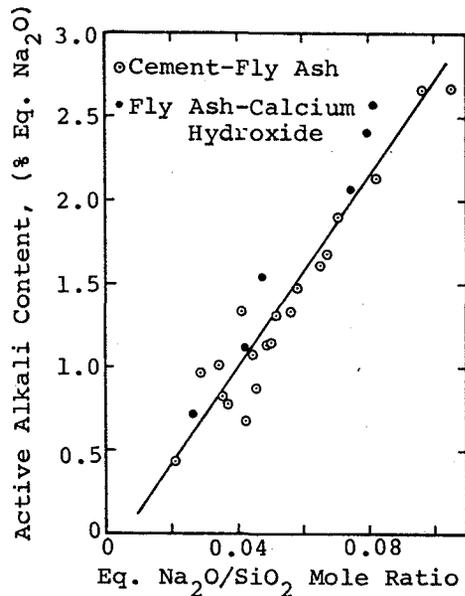


Figure 3. Relationship between concentration of ultimate active alkalis and N/S mole ratio

as an additional admixture for boosting SiO₂ content.

5. CONCLUSION

It is recommended that further research be conducted on the standard test procedure to explicitly define the influence of the composition of a given reacting system on the measured active alkalis. Until such work is completed three measures are suggested for determining or estimating the active alkalis in the cement-fly ash combination. First, the amount of calcium hydroxide to be used for the test should be determined in accordance with the composition of the job cement and the percentage of fly ash to be used for replacement. Secondly, the empirical regression equation developed in this study should be used to estimate the concentration of active alkalis from the known N/S mole ratio of the reacting system. Finally, the total alkali content, instead of available alkali content, should be used as a conservative measurement of the alkali content of Class C and borderline Class C-Class F fly ashes.

6. REFERENCES

- [1] Buttler, F. G., S. R. Morgan and E. J. Walker, Studies on the Rate and Extent of Reaction Between Calcium Hydroxide and Pulverized Fuel Ash at 38°C, Proceedings of the Fifth International Conference on Alkali-Aggregate Reaction in Concrete, Cape Town, South Africa, 1981, S252/38.
- [2] Lee, C., S. Schlorholtz and T. Demirel, Available Alkalies in Fly Ash, Materials Research Society Symposia Proceedings, Vol. 65, 1985, 125-129.