

PROCEEDINGS OF THE SECOND INTERNATIONAL CONGRESS ON  
ENVIRONMENTAL GEOTECHNICS/OSAKA/JAPAN/5-8 NOVEMBER 1996

# Environmental Geotechnics

*Edited by*

MASASHI KAMON

*Kyoto University, Japan*

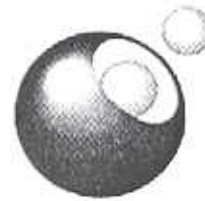
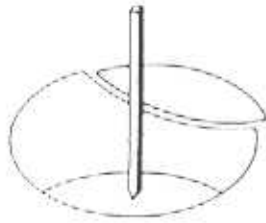
VOLUME 2



A.A. BALKEMA/ROTTERDAM/BROOKFIELD/1996



Organized by The International Society for Soil Mechanics and Foundation Engineering  
and The Japanese Geotechnical Society



*The texts of the various papers in this volume were set individually by typists under the supervision of each of the authors concerned.*

Authorization to photocopy items for internal or personal use, or the internal or personal use of specific clients, is granted by A.A. Balkema, Rotterdam, provided that the base fee of US\$1.50 per copy, plus US\$0.10 per page is paid directly to Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, USA. For those organizations that have been granted a photocopy license by CCC, a separate system of payment has been arranged. The fee code for users of the Transactional Reporting Service is: 90 5410 848 7/96 US\$1.50 + US\$0.10.

Published by

A.A. Balkema, P.O. Box 1675, 3000 BR Rotterdam, Netherlands (Fax: +31.10.4135947)

A.A. Balkema Publishers, Old Post Road, Brookfield, VT 05036-9704, USA (Fax: +1.802.2763837)

For the complete set of three volumes, ISBN 90 5410 848 7

For Volume 1, ISBN 90 5410 849 5

For Volume 2, ISBN 90 5410 850 9

For Volume 3, ISBN 90 5410 851 7

© 1996 A. A. Balkema, Rotterdam

Printed in the Netherlands

## Hydration mechanisms of fly ash stabilized by lime

Supakij Nontananandh

*Department of Civil Engineering, Kasetsart University, Bangkok, Thailand*

Masashi Kamon

*Disaster Prevention Research Institute, Kyoto University, Japan*

**ABSTRACT:** Many current researches have recognized that coal fly ashes stabilized by cement and/or lime steadily gain strengths over time due to the pozzolanic reaction. The major attraction in using this material in pavement or grouting work is that the structure will be progressively stronger over its design life. Understanding of certain reaction mechanisms significantly provides improvement on fly ash stabilization to a satisfactorily high level. The experimental studies presented in this paper have been devoted to elucidate hydration mechanism and major reaction products of lime-stabilized fly ash mixtures. Evaluation of hardening effects was performed based on the compressive strength test and by means of the physico-chemical tests. It is found that hardening mechanism can be improved when a certain proportion of chemical additives such as aluminum sulfate and sodium carbonate are blended into the hydrated lime. Consequent improvement on strength is due to the enhancement of hydration by a through-solution mechanism. Strength development is closely related to chemical compositions of fly ash, appropriate type and amount of stabilizer, types, degree of crystallization and morphology of reaction products, and changes in their microstructures during the course of reactions.

### 1 INTRODUCTION

Coal fly ashes (fly ashes) are presently generated in large quantities worldwide due to increasing demand for energy consumption. Fly ash utilization as construction materials can concomitantly compromise concerns for technical and economical feasibility along with the environmental control. Potential uses for this material include a design of lime-cement-fly ash for runway pavement (Jefts, 1986), remedial works on the leachate problems by fly ash-cement grouting, materials for concrete dam and recently for roller compacted concrete (RCC) dam, and fly ash-bentonite containment walls (Cabrera et al., 1994).

Concerning technical advantages, fly ashes accelerate the early strength of cement, reduce heat of hydration, improve workability of concrete, and improve resistance to sulfate

attack and chloride ion penetration. In the presence of hydrated lime, coal fly ashes contribute to long-term strength due to the carbonation and pozzolanic reactions.

For hydration mechanisms of the lime-pozzolana mixtures, several hypotheses have been proposed. Uchikawa and Uchida (1980, 1986) found that the initial rate of hydration of the  $C_3A$ -lime-gypsum mixtures was activated by pozzolanic material. Chemical reactivity was enhanced by its characteristics such as specific surface area, exchange capacity of cation, and glass phase contents. Enhancement of hydration in this case is basically due to a topochemical mechanism.

Preliminary study on the stabilization of lime-fly ash mixtures by Kamon et al. (1988) indicated that changes in microstructures were due to certain hardening effects. Significant improvement on strengths could be observed



Table 1a Chemical compositions of fly ashes

Materials	Compositions (%)								
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>
Fly Ash I	49.3	22.0	4.40	5.40	1.10	2.01	1.20	1.23	0.70
Fly Ash II	56.9	32.7	1.70	0.50	0.30	1.12	0.11	1.74	<0.1

Table 1b Selected national standard specifications for fly ashes used in concrete and properties of fly ashes used in this study

Requirement	Fly ash		Australia	Canada		India	Japan	UK	USA	
	I	II		Class C	Class F				Class C	Class F
Ignition loss, max%	1.1	5.1	5.0	12.0	6.0	12.0	5.0	7.0	12.0	6.0
SO <sub>3</sub> , max %	0.7	0.1	-	5.0	5.0	3.0	-	5.0	5.0	5.0
MgO, max %	1.1	0.3	5.0	-	-	5.0	5.0	5.0	5.0	5.0
Alkali metal as Na <sub>2</sub> O, max%	2.0	1.1	-	-	-	1.5	-	1.5	1.5	1.5
SiO <sub>2</sub> , min %	49.3	56.3	-	-	-	35.0	45.0	-	-	40.0
SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub> +Fe <sub>2</sub> O <sub>3</sub> , min%	75.7	91.3	-	-	-	70.0	70.0	70.0	-	50.0
Specific surface area, m <sup>2</sup> /kg	310	330	-	-	-	320	270	-	-	-

when lime was mixed with some chemical additive such as sodium carbonate and aluminum sulfate. However, conceptual views on how strengths are improved, especially in the presence of this type of additives, are unclear and thus need to be further substantiated. It is, therefore, our main objective in this study to elucidate hydration mechanism of coal fly ashes stabilized by lime, in order to achieve strengths applicable as road subbase and base materials.

## 2 EXPERIMENTAL PROCEDURE

### 2.1 Materials

Two types of fly ashes, designated as fly ash I and fly ash II, were used. According to ASTM C-618, these fly ashes are classified as low-lime (class F) fly ashes. Both types of fly ash consist mostly of glassy, spherical particles as observed by scanning electron microscopic observation. X-ray diffraction patterns of the untreated ashes clearly reflected peaks corresponding to quartz (SiO<sub>2</sub>) and mullite (3Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>). Material compositional analysis revealed that Si, Al, and Ca are identified as dominant elements for fly ash I, while Si and Al predominate in fly ash II. Chemical compositions of fly ashes are given in Table 1a. As illustrated in Table 1b, the

properties of fly ashes used are consistent with the standard specifications of other countries.

### 2.2 Specimen preparation and test

Specimens were prepared by mixing fly ashes with hydrated lime and lime-based stabilizer, using mix proportions of 10% and 20% by total weight. Lime-based stabilizer used as a hardening material consists of 70% Ca(OH)<sub>2</sub>, 18% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 12% Na<sub>2</sub>CO<sub>3</sub>. In order to obtain a uniform consistency of freshly mixed fly ash with workability (flow value) within a range of 150-190 mm, it was decided to control the mixtures with a mixing water of 60% by total weight. Mixing conditions are summarized in Table 2.

Mixing and preparation of specimens were carried out according to the method of making and curing noncompacted - stabilized soil specimens (JSF T-821). Fly ash fresh pastes were put in a mold for obtaining a cylindrical specimen of 5 cm in diameter and 10 cm in length. After approximately 18-24 hours, the specimens were demoulded and cured in a constant-temperature room (20°C, 80% relative humidity) until testing. Compressive strength tests were carried out after the curing periods of 3, 7, 28, and 90 days. Some were available for

Table 2 Strength of the fly ash-stabilized mixtures

Mixtures Symbol	Materials & Contents		Compressive Strength (MPa)				
	fly ash	stabilizer	3 days	7 days	28 days	90 days	2.75 years
MIX-1	90% ash I	10% lime	0.16	0.77	0.48	2.63	6.40
MIX-2	80% ash I	20% lime	0.08	0.18	1.10	5.15	*
MIX-3	90% ash I	10% LBS	0.23	0.65	7.14	7.17	*
MIX-4	80% ash I	20% LBS	0.49	1.07	10.11	11.01	*
MIX-5	90% ash II	10% lime	0.12	0.13	0.28	0.28	2.48
MIX-6	80% ash II	20% lime	0.06	0.09	0.46	0.57	*
MIX-7	90% ash II	10% LBS	0.07	0.17	0.84	2.79	*
MIX-8	80% ash II	20% LBS	0.08	0.31	4.38	5.15	12.30

Note: LBS stands for lime-based stabilizer which is composed of 70% lime, 18%  $Al_2(SO_4)_3$ , and 12%  $Na_2CO_3$ .

\* stands for no observed data

the test almost after 3 years. In order to elucidate hydration mechanisms and major reaction products, X-ray diffraction analysis (XRD), scanning electron microscopic observation (SEM) and energy dispersive X-ray microanalyzer (EDX) were performed on the failure specimens after strength test.

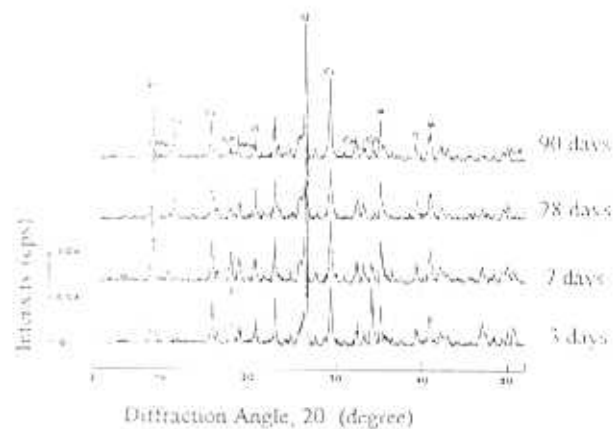
### 3 RESULTS AND DISCUSSION

#### 3.1 Strengths of fly ash mixtures

Table 2 shows comprehensive strengths of all mixtures. It is most likely that strengths of lime-stabilized mixtures were developed slowly in the early age and steadily increased as curing time increased. For such mixtures as MIX-1, MIX-5 and MIX-6, strength development appears to be more pronounced after 33 months. Actually, a relatively high strength in long term elucidates the potential for utilization of the stabilized fly ash as subbase for road.

For the same mixing condition, the mixtures of fly ash I gave considerably higher strengths than those of fly ash II in all respects. It is, however, can be noticed that at long term the fly ash II mixtures can develop strengths comparable to those of fly ash I mixtures. As shown in Table 2, the 2.75-year specimen of MIX-5 and MIX-8 developed strengths to a certain level of the 90-day strengths of MIX-1 and MIX-4, respectively.

As a material for road base purpose, it is recommended that a mixture should gain 10-day strength of 0.7 MPa for a lower base and 1.0 MPa for upper base, without yielding a loss in strength. It is found that the strengths were



Cc: Calcium carbonate    Ch: Calcium aluminate hydrate  
 Ch: Calcium hydroxide    Cs: Calcium Silicate hydrate  
 Et: Etringite            Q: Quartz  
 M: Mullite                Ms: Monosulfate

Figure 1 XRD patterns of 20% lime-based-stabilized fly ash I at various curing periods.

markedly improved in agreeable with the recommendation when lime-based stabilizer was used. For example, the 28-day strength of fly ash I, MIX-1 and MIX-3, are 0.48 and 7.14 MPa, while, those of fly ash II, MIX-6 and MIX-8, are 0.46 and 4.38 MPa, respectively. In this study, the stabilizer was found more active in the fly ash I mixtures than in the fly ash II mixtures. This indicates that chemical compositions of the original ash affect the hardening in the resultant mixtures.

The evidence of strength development thus brings to light some essential roles by which aluminum sulfate and sodium carbonate in combination with lime contributes to strength of fly ash mixtures. It is believed that lime-based stabilizer accelerates hydration of ash through



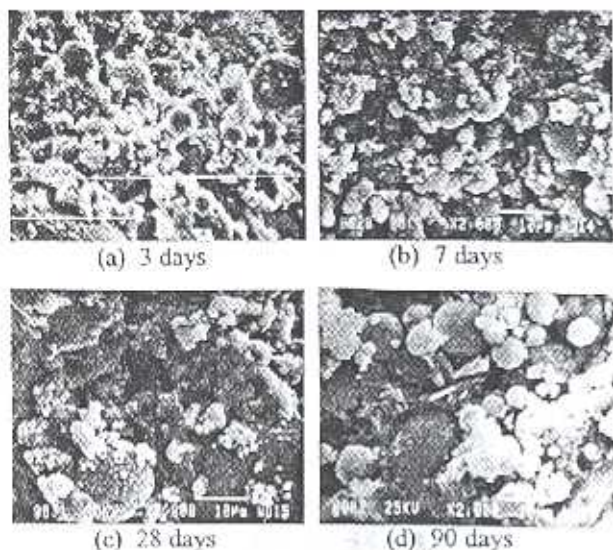


Figure 2 Typical SEM micrographs of 20% lime-stabilized fly ash I at specified curing periods of 3, 7, 28, and 90 days

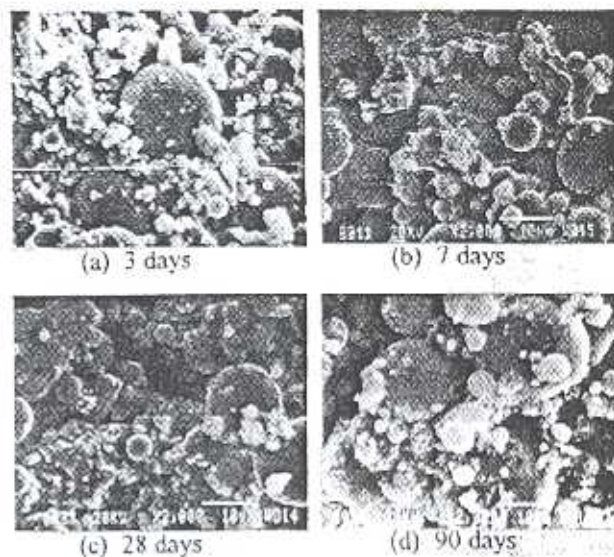


Figure 4 Typical SEM micrographs of 10% lime-stabilized fly ash II at specified curing periods of 3, 7, 28, and 90 days

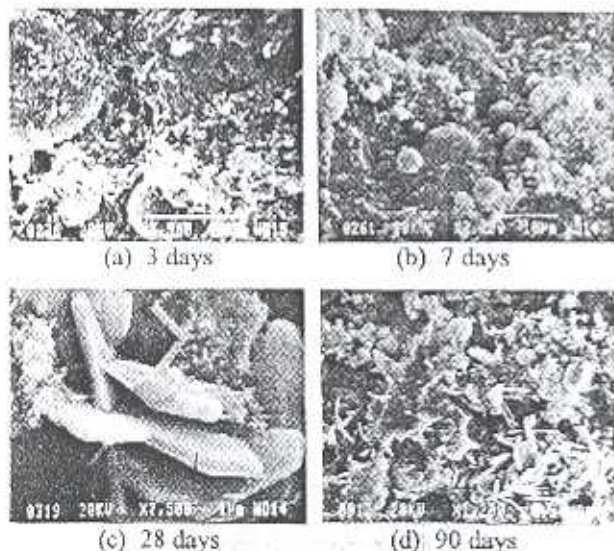


Figure 3 Typical SEM micrographs of 20% lime-based-stabilized fly ash I at specified curing periods of 3, 7, 28, and 90 days

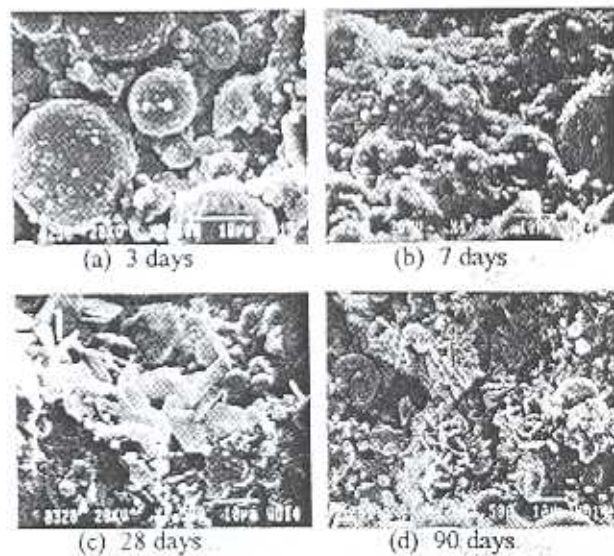


Figure 5 Typical SEM micrographs of 20% lime-based-stabilized fly ash II at specified curing periods of 3, 7, 28, and 90 days

particular mechanisms. Further discussion is presented to substantiate this assumption.

### 3.2 Changes in mineral composition and microstructures in relation to strength development

Typical XRD patterns of the fly ash I mixed with lime-based stabilizer (Figure 1) show reduction of the crystalline components of fly ash and hydrated lime. They converted into reaction products which can be identified as

calcium silicate hydrate (CSH), calcium aluminate hydrate (CAH), ettringite, and calcium carbonate ( $\text{CaCO}_3$ ). Mixtures having superior strengths exhibit larger amounts of these major reaction products, while those with low strength exhibit weak diffractions of such cementitious materials but strong peaks of hydrated lime. For lime-fly ash I, no marked changes in ash particles and the overall microstructures could be seen even at long term, as illustrated in Figures 2a - 2d. The



reactions in this case seemingly proceed in a slow rate. Conversely, for lime-based stabilizer, the reaction products were abundantly produced on the fly ash surface, filling up the voids which were previously filled with pore water (Figure 3).

Conversion of ettringite crystals into hexagonal cardboard-shape monosulfates could be observed (Figures 3b-3c). Accordingly, fly ash particles virtually changed into smaller in sizes after 28 days. Figures 3c and 3d reveal that fly ash particles act as spherical cores where upon reactions products are formed extensively. The combination of reaction products such as this resulted in a higher rigidity.

In agreement with the strength test results, there were no marked changes for fly ash II when mixed with lime (Figures 4a-4d). Some remained unreacted even at long time. When lime-based stabilizer was used, changes in microstructures could be observed (Figures 5a-5d). However, there are some distinct differences between the developed microstructures of fly ash I and fly ash II mixtures.

First, monosulfate phases formed in fly ash II mixtures are the hexagonal rosette features (Figure 5d), while, in fly ash I mixtures the hexagonal cardboard features are formed (Figure 3c). Second, some inert fly ash II particles remain unreacted and inherently impede in a dense structure (Figure 5d).

It can be concluded that fly ash I consists of more active aluminosilicate particles than fly ash II. In addition, substantial changes in microstructure into a denser texture contribute to strength development of the lime-fly ash stabilized materials.

### 3.3 Hydration mechanisms of fly ash mixtures

Based on investigations of changes in microstructures and their morphology in terms of hydration time, the conceptual pictures regarding the reaction mechanisms can be highlighted. The essential roles of sodium carbonate and aluminum sulfate as a chemical additive for lime can be asserted using the reacting solid particle models as illustrated in Figure 6. Based on the results of strength test and microscopic observations, reactivities of the

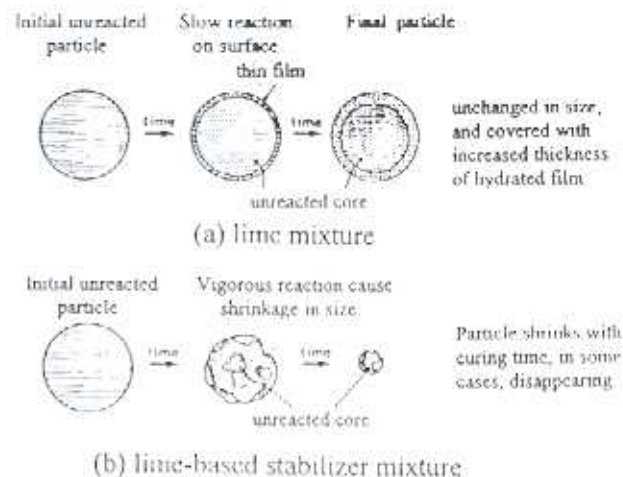


Figure 6 Reaction mechanisms of reacting fly ash particles for: (a) in lime mixtures, and (b) in lime-based stabilized mixtures

mixtures can be categorized by the following order, lime-based stabilized ash  $\gg$  lime-stabilized ash  $>$  hydrated ash. In all cases for the same mixing condition, fly ash I gains superior reactivity than fly ash II.

Beneficial effects concerning an addition of additives into lime are attributed to three main reasons.

First, the chemicals added improve reaction by increasing the rate of solubility of fly ash particles; thus, increase the rate of initial hydration and pozzolanic reaction in long term.

Second, in addition to this, major reaction products such as CSII, ettringite and monosulfate are richly formed and gradually strengthened structures as reaction progresses.

Third, cementation is activated due to the presence of sodium carbonate. Formation of  $\text{CaCO}_3$  substantially fills the voids and thus provides additional cementation of the phases.

In the lime-fly ash system, ash particles initially react slowly with hydrated lime. Thin hydrate films, presumably a CSII phase, are formed, covering the unreacted cores. These protective layers then retard further reaction of fly ash particles.

However, as curing time increases, thickness of the hydrate film increases slightly, probably due to a diffusion of  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ , and  $\text{H}^+$  into the inner cores (Figure 6a). Through such reaction mechanisms, the particles sizes are mostly unchanged as previously illustrated by SEM micrographs.



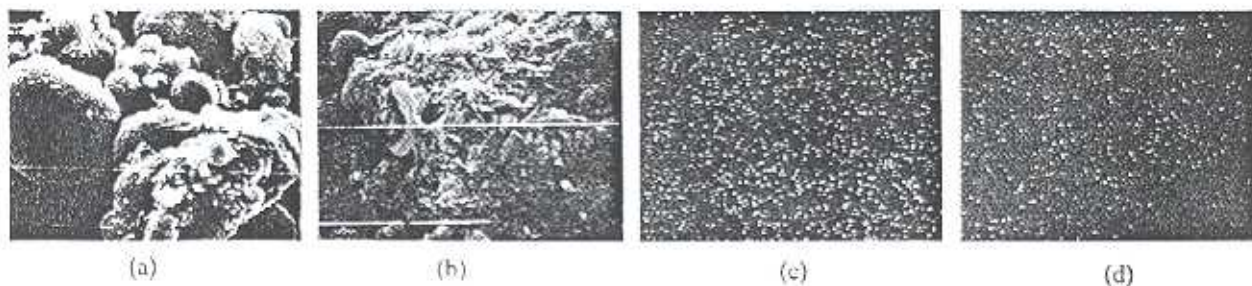


Figure 7(a) Dissolution and agglomeration of fly ash in lime-based mixtures  
 7(b) SEM micrographs of 10% lime-based stabilized fly ash at 3 days  
 7(c) X-ray mapping of Ca element on the scanned view of 7(b)  
 7(d) X-ray mapping of Si element on the scanned view of 7(b)

Conversely, the particles seem to dissolve vigorously at the very beginning when sodium carbonate and aluminum sulfate are present in the mixtures (Figure 6b).

As clearly seen in Figure 7a, surfaces of the spherical ashes are leached out and changed into irregular shapes, while some grains are agglomerated into a cluster. Dissolution of fly ash in this case can be further substantiated by an investigation of the constitutive elements on the surface. It is noted that fly ash is the only source of silicon. Therefore, as illustrated in Figures 7b-7d, the distribution of Si and Ca over the whole surface will assert to the fact that silicate as well as aluminate minerals dissolve into the pore solution, and thus activate hydration of the lime-based-fly ash system, resulting in the development of strength. As can be expected, such observations were not found in the lime-fly ash systems.

#### 4 CONCLUSIONS

Based on the experimental study, the main results are concluded as follows:

1. Strength development of the coal fly ash is substantially influenced by several factors, namely, reactivity of original fly ash, type and amount of stabilizer and mixing condition.
2. Strengths have improved in relation to the types of hydration products and their morphological characteristics.
3. The major reaction products which contribute to strengths are calcium silicate hydrate, calcium aluminate hydrate, ettringite and monosulfate and calcium carbonate.

4. Certain proportion of lime, sodium carbonate and aluminum sulfate markedly improve the reactions of the lime-fly ash mixtures by an increase in dissolution of ashes and starting materials, acceleration of the hydration and pozzolanic reactions, simultaneous activation of the carbonation.

5. Hypothesis in relation to strength developing mechanisms is proposed. Strength of the fly ash mixtures can be improved when hydrations are enhanced by the through-solution mechanism.

6. Strengths of the successful mixtures of lime-stabilized fly ash show promise for as geomaterials such as road base and subbase.

#### REFERENCE

- Cabrera, J.G. and Woolley, G.R. (1994); "Fly Ash Utilisation in Civil Engineering", *Environmental Aspects of Construction with Waste Materials*, edited by Goumans J.J.J.M. et al., pp.345-356.
- Jefts, A.R. (1986). "New Runway Takes Off", *Civil Engineering*, ASCE, pp.47-49.
- Kamon, M., Nontananandhi, S. and Tomohisa, S. (1988); "On Lime-Stabilized Fly Ashes by X-ray Microanalyzer in relation to Strength Development", *Proc. of the 43th JSCE Conference*, Hiroshima, Japan, pp.168-169.
- Uchikawa, H. and Uchida, S. (1980), "Influence of Pozzolana on the Hydration of  $C_3A$ ", the 7th International Congress on Chemistry of Cement, Sub-theme IV, Paris, pp.24-29.
- Uchikawa, H. and Uchida, S. (1986), "Effect of the Character of Glass Phase in Bleeding Components on their Reactivity in Calcium Hydroxide Mixture" the 8th Int Congress on Chemistry of Cement, Rio de Janeiro, Sub-theme 3.2, pp.245-250.