Philippine Engineering Journal (1995) XVI (1): 49-72

POZZOLANIC BEHAVIOR OF MT. PINATUBO EJECTA UNDER NATURAL AND ACCELERATED CURING CONDITION

Pablo A. Jorillo, Dr. Eng.
Associate Professor

Benjamin D. Verdejo
Head/Assistant Professor

Department of Civil Engineering
Integrated Research and Training Center
Technological University of the Philippines
San Marcelino, Manila

ABSTRACT

This paper describes the results of the study on the evaluation of the pozzolanic behavior of Mt. Pinatubo ejecta under natural and accelerated curing conditions. The study is essentially a developmental research aimed in providing a comprehensive characterization of the volcanic ejecta in comparison with the local fly-ash. Two types of accelerated curing were examined viz., high pressure steam curing and boiling-cooling method. Various types of ejecta materials and percentage cement replacements were investigated to determine the optimum type and proportion in a cement based mortar matrix based on the criteria of strength and dimension stability.

INTRODUCTION

Pozzolanic materials are utilized essentially as active addition to the clinker of cement primarily for technological, economical and environmental reasons. Technological, in a sense that, it can modify the properties of cement, improve the durability characteristics and its resistance to aggressive agents. Economical, because addition of pozzolan reduces the quantity of cement which in turn, saves foreign reserves needed for cement importation and fuel required for local cement production. Environmental, because utilization of pozzolanic material such as fly-ash, rice husk ash and volcanic ash reduces waste and ill-wanted materials. These reasons alone fully justify the utilization of active addition of pozzolan to cement in construction, cement and concrete industries (Talero, 1990).

Pozzolans are siliceous or alumino-siliceous materials which in finely divided form and in the presence of moisture will chemically react with alkali and alkaline earth hydroxides to form compounds with cementitious properties (ASTM, 1993). Volcanic ash, lava deposits, active clay, santorin earth and trass are few of the many natural pozzolans which have been in used for over thousands of years in making cementitious products. With the 1991 eruption and continued activity of Mt. Pinatubo, the peripheral provinces, e.g. Zambales, Pampanga, and Tarlac, suffered heavy damages due to pyroclastic and lahar (i.e., mass of volcanic debris and water) movement. It is estimated that Mt. Pinatubo ejected a total volume of 8-10 billion cubic meters of pyroclastic and tephra fall deposits in these provinces leaving havoc and destruction.

These pyroclastic and lahar deposits are currently being studied and developed for various applications in agriculture, ceramics, foundry works, entomology, soil engineering, and civil engineering works (Bernardo, 1994; Almeniana, 1992; Pagbilao et al., 1992, Mendoza et al., 1992; Acda et al., 1992; Metra et al., 1992). Lahar and volcanic ash are basically pumiceous material consisting of feldspar, quartz, and amphiboles which are essentially silicate materials rich in aluminum, calcium, potassium and sodium (Shimizu et.al., 1993). Initial study presented by Shimizu and Jorillo (1992) at the International Scientific Conference on Mt. Pinatubo showed that the lahar material is a highly siliceous material with relatively good degree of amorphousness, and thus was recommended as pozzolanic material for partial cement replacement. Currently , parallel experimental studies on lahar material are being undertaken by various research institutions like DOST-ITDI, UP-BRS, DOST-FPRDI, TUP-IRTC, DPWH-BRS and PHILCEMCOR (Alabastro, 1994). However, there are still very few published reports that can be found on the pozzolanic behavior of the Mt. Pinatubo ejecta. Initial reports of TUP-Nihon University (Schimizu, Jorillo 1992), Bureau of Soils and Water Management (Micosa et.al., 1992), PHILCEMCOR (Espina, 1994) and FPRDI (Ignacio, U., et al., 1994) already indicated the suitability of Pinatubo ejecta as pozzolan. In spite of these initial reports, no in-depth information are available on the contribution of Pinatubo ejecta pozzolan to the following properties of a given concrete or mortar;

(a) porosity, permeability, watertightness
(b) long-term strength development
(c) dimension stability, shrinkage/expansion properties,
(d) resistance to severe environmental conditions and,
(e) resistance to alkali-aggregate reaction.

Furthermore, these studies already indicated the varied pozzolanicity of lahar, and yet no recommendation was presented on how to evaluate the suitability of a given lahar material as a pozzolan under a shorter range of testing time. Hence, it is very clear that aside from a comprehensive characterization of Pinatubo ejecta, an optimum accelerated method of curing need to be examined so that the suitability of lahar as a pozzolan or as an aggregate can be evaluated at a shorter period of time. Due to the lack of published information on this type of pozzolan this experiment was initiated to:

(a) determine the optimum percentage substitution of cement by lahar under natural and accelerated curing conditions
(b) determine the response of various types of Pinatubo ejecta under different modes of accelerated curing condition
(c) determine the shrinkage properties and dimension stability of cement mortar with lahar as partial cement substitute

Background on the Properties of Natural Pozzolan

Natural pozzolan are materials which exhibit pozzolanic properties in their natural state and, it includes incoherent and compact siliceous rocks of volcanic origin and material from skeletons of living organism (Turriziani, 1980). These types of pozzolans are classified as volcanic/zeolitized glass and pozzolanic tuffs of organic origins. The volcanic ash, lava deposits, and lahar ejected by the Mt. Pinatubo can be classified under the volcanic glass grouping (Delos Reyes, 1994).

The paper presented by Delos Reyes (1994) of PHILVOCS at the 1993 ITIT (International Symposium on Utilization Technology of Volcanic Ejecta) revealed that initial tephra fall deposits (June-July 1991) were predominantly andesite scoria, and components of paroxysmal eruptions were phenocryst-rich and phenocryst-poor dacite pumice fragments. During the 1991-1992 activity, pyroclastic flow (sandy and pumiceous) deposits was estimated at a volume of 5-7 km^3. Flow observed from Mt. Pinatubo are differentiated as hyperconcentrated streamflows and debris flow. The hyperconcentrated flows are dense suspension of sediment in water with sediment content of about 40-60%. Debris flow, on the other hand, appears as liquefied slurry with consistency comparable to wet concrete and with fragments ranging from clay to boulder size. These observations confirmed the nature of Pinatubo ejecta in terms of its geological history and mineralogical properties.

The chemistry of pozzolanic material in a cement matrix involves the chemical reaction of the reactive silica (SiO_2) with lime ($Ca(OH)_2$) to form calcium silicate hydrates which are believed to be primarily responsible for the strength improvement. James and Rao (1986) explained the silicates formed are of the kind, *CSHI* and *CSHII*, and the reaction sequence may be illustrated as,

$$Ca(OH)_2 + SiO_2 = CSHI + CSHII$$

$$C_3S \text{ or } C_2S \text{ (Portland cement)} + H_2O = CSH + Ca(OH)_2$$

$$\textbf{Portland cement} + \textbf{Pozzolan} + H_2O = CSH + \textbf{unreacted } SiO_2$$

$$\text{where } C_3S = 3CaOSiO_2 \text{ and } C_2S = 2CaOSiO_2$$

$$CSH = CSHI + CSHII$$

$$CSHI = CaO_{0.8-1.5}SiO_2(H_2O)_{1.0-2.5}$$

$$CSHII = CaO_{1.5-2.0}SiO_2 2(H_2O)$$

Other properties of mortar or concrete with pozzolan as active additions are presented by Price (1975) and Mehta (1981). Among the advantages in the use of pozzolanic material are improvement of workability, watertightness, resistance to sulfate soil, seawater, acid mediums and alkali-aggregate reactions. However adverse effects to concrete/mortar such as reduced rate of hardening, shrinkage, increased water requirements and low resistance to alternate wet-dry cycles or freezing and thawing may result if an inferior pozzolan or excessive proportions are used.

EXPERIMENTAL PROGRAM

Coverage of Experiment

In order to provide a more comprehensive information on the pozzolanic behavior of the Pinatubo ejecta, the experimental program was divided into four series of experiments, namely,

Series-1: Evaluation of properties of cement mortar with various pozzolan under natural curing condition.

Series-2: Evaluation of properties of cement mortar with different types of pozzolanic material under high pressure and high temperature (autoclave) method of steam curing.

Series-3: Evaluation of properties of cement mortar with various pozzolans under boiling method and accelerated curing.

Series-4: Evaluation of the dimension stability and shrinkage properties.

A comparative study of this type of pozzolan with the Calaca, Bataan Fly-ash was also conducted in order to gage the pozzolanic properties under various method of curing. Variables considered in this study are enumerated in Table 1.

Materials and Specimen Preparation

Type-1 Portland cement was used as binding medium, and the physical and mechanical properties are shown in Table 3 and 4. An ordinary river sand from Angono with a maximum size of 0.60 mm, specific gravity of 2.52, and absorption of 1.24% was used as fine aggregate. For the pozzolanic material, two types were examined, namely, Fly-ash and Pinatubo ejecta pozzolan. The fly-ash came from NPC coal plant in Calaca, Bataan. As for the natural pozzolan, selected sites in Pampanga were chosen, that is, Mabalacat and Pasig Potrero. Various types and forms of the lahar debris were collected from this two sites, viz., three groups of pumicite stones (P1, P2, P3), three types of lahar sand (L1, L2, L3) and two groups of slurry sediments (S1, S2). These lahar materials were ballmilled and passed through 0.074 mm sieves. The chemical and physical properties of the mineral admixtures as determined per ASTM are shown in Table 2 and 3, respectively.

The adopted mix proportion has a water-cement (W/C) of 65%, sand-cement (S/C) ratio of 2.75 and a mineral admixture dosage of 5, 10, 20, 30, 40 and 50% substitution by weight of cement. The mortar were mixed in a 5-liter Hobart mixer per ASTM C-305. The designed workability of the control mortar was 200-220 mm, which was sufficient enough to measure any increase or decrease in the workability of mortar due to the active addition of pozzolan. The mixture were cast its respective mold and stored in laboratory condition of $25^{O}C$ and 60-80% relative humidity for 24 hours. After which the specimens were demolded and stored in their corresponding curing tanks.

Table 1
Variable considered in the Experimental Programme

PARAMETER	VARIABLES	RANGE	LIMITATIONS
Cement Binder	(W/C) Water-Cement ratio	W/C = 65%	ASTM Type 1 Portland
Aggregates	(S/C) Sand-Cement ratio	S/C = 2.75	Angono river sand
Mineral Admixture	Site	Sample Identification	Code Identification
A. Lahar Sample	1. Mabalacat 2. Pasig Potrero	1. L1, L2, P1 2. L3, P2, P3, Si, S2	(L) Lahar sand type (P) Pumicite stones (S) Slurry sediments
B. Fly-ash	1. NPC Calaca, Bataan	1. FA	(FA) Fly ash
Mineral % substitution by wt of Cement	(Mineral/C+Mineral) %	5, 10, 20, 30, 40, 50%	All series: 0.30% L3, P3, FA series: 0-50%
Curing Method	1. Natural Curing (ages)	7, 28, 63, 91 days	L3, P3, FA series
	2. Autoclaving	Conditions 1. 15 kgf/cm^2 - 3 hours 2. 15 kgf/cm^2 - 6 hours 3. 15 kgf/cm^2 - 9 hours 4. 25 kgf/cm^2 - 3 hours	 1. All Series 2. L3, P3, FA series 3. L3, P3, FA series 4. L3, P3, FA series
	3. Boiling Cooling (cycles)	5, 10, 20, 30 cycles	All Series

Method of Curing Regime and Property Test

There are two major types of curing adopted in the study, namely, natural and accelerated method. Natural curing allowed the specimens to reach their normal strength under natural curing condition, i.e., specimens were cured in 25-27^{O}C water bath and strengths were evaluated at ages of 7, 28 and 63 days. Whereas, accelerated curing was executed through the aid of increased temperature, increased pressure, and increased in/out movement of water in the

Table 2
Oxide Analysis of Cement and Mineral Admixtures (Pozzolans)*

LOCATION	CODE	TYPE	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O
1. Mabalacat	P1	Pumicite stones	61.7	17.6	4.3	4.3	1.2
	L1	Lahar sand	61.3	18.1	4.6	4.2	1.5
	L2	Lahar sand	64.5	17.4	4.4	4.1	1.5
2. Pasig Potrero	P2	Pumicite stones	62.9	18.1	4.6	4.4	1.5
	P3	Pumicite stones	60.3	18.6	5.8	4.8	0.9
	L3	Lahar sand	63.1	17.9	4.4	4.1	1.4
	S1	Slurry sediments	64.4	18.0	5.0	4.3	1.6
	S2	Slurry sediments	61.3	19.7	6.2	4.7	1.0
3. NPC Bataan	FA	Fly-ash	81.1	15.5	1.0	0.1	0.6
4. Cement	OPC	ASTM Type 1 Portland	21.8	5.1	3.1	0.2	0.4

* Oxide analysis per ASTM method

Table 3
Physical Properties of Cement and Mineral Admixtures (Pozzolans)*

PROPERTIES	Pumicite Stones			Lahar Stands			Slurry Sediments		Fly-Ash	Cement
	P1	P2	P3	L1	L2	L3	S1	S2	FA	OPC
1. Specific Gravity	2.40	2.46	2.44	2.44	2.50	2.50	2.40	2.42	2.13	3.12
2. Setting Time										
Initial (h-min)	1-22	1-12	1-18	1-06	2-10	1-52	1-50	1-46	1-51	1-26
Final (h-min)	3-16	3-20	3-12	3-32	3-26	3-12	3-25	3-18	3-44	3-11
3. Water Requirements (%)	103.8	108.5	104.0	106.5	112.0	103.8	108.0	102.0	98.0	100.0
4. Pozzolanic Activity Index with Cement (%)	87.5	92.3	92.7	85.7	85.5	91.3	107.1	96.4	118.5	100.0

* Physical properties tests per ASTM Standards

Table 4
Compressive Strength Blended Cement Mortar
Under Different Methods of Curing

CURING METHOD	(%) POZZ	PUMICITE P1	PIMICITE P2	PUMICITE P3	LAHAR L1	LAHAR L2	LAHAR L3	SEDIMENT S1	SEDIMENT S2	FLY-ASH
1. Natural Curing 28 days (50x50x50)	0	250	250	250	250	250	250	250	250	250
	5	248	256	227	251	238	271	238	269	285
	10	220	271	253	225	235	259	289	241	294
	20	240	241	213	205	273	229	225	246	284
	30	-	-	209	-	-	189	-	-	285
2. Autoclaving 1.5 kgf/cm^2 for 3 hours (50x50x50)	0	212	212	212	212	212	213	212	212	212
	5	213	208	211	203	213	227	243	268	265
	10	197	243	229	219	217	241	274	268	275
	20	197	232	214	237	248	236	230	250	317
	30	256	251	276	279	249	231	242	278	308
3. Boiling-Cooling 5 cycles 50ϕ x 100	0	208	208	208	208	208	208	208	208	208
	5	202	189	210	197	189	224	231	231	238
	10	196	222	214	215	208	223	259	218	238
	20	187	191	175	214	198	226	201	221	234
	30	169	215	182	206	188	203	210	166	237
4. Boiling-Cooling 10 cycles (50ϕ x 100)	0	214	214	214	214	214	214	214	214	214
	5	216	227	240	232	215	240	269	265	271
	10	228	250	223	235	208	203	241	256	272
	20	206	234	183	232	232	232	239	238	261
	30	199	209	172	200	205	233	212	176	249

cement mortar. Two types of hydrothermal accelerated method of curing were adopted in the experimental program, viz., autoclaving, and boiling-cooling method.

High pressure steam curing or autoclaving method was used as one method of accelerated curing. Pressures of 15 kgf/cm^2 (212 psi) and 25 kgf/cm^2 (355 psi) under a retention time of 3, 6, and 9 hours was applied to blended cement mortar specimens. Execution of the autoclave method of curing was similar to the test method recommended by ASTM C-151 (cf. Figure 1)

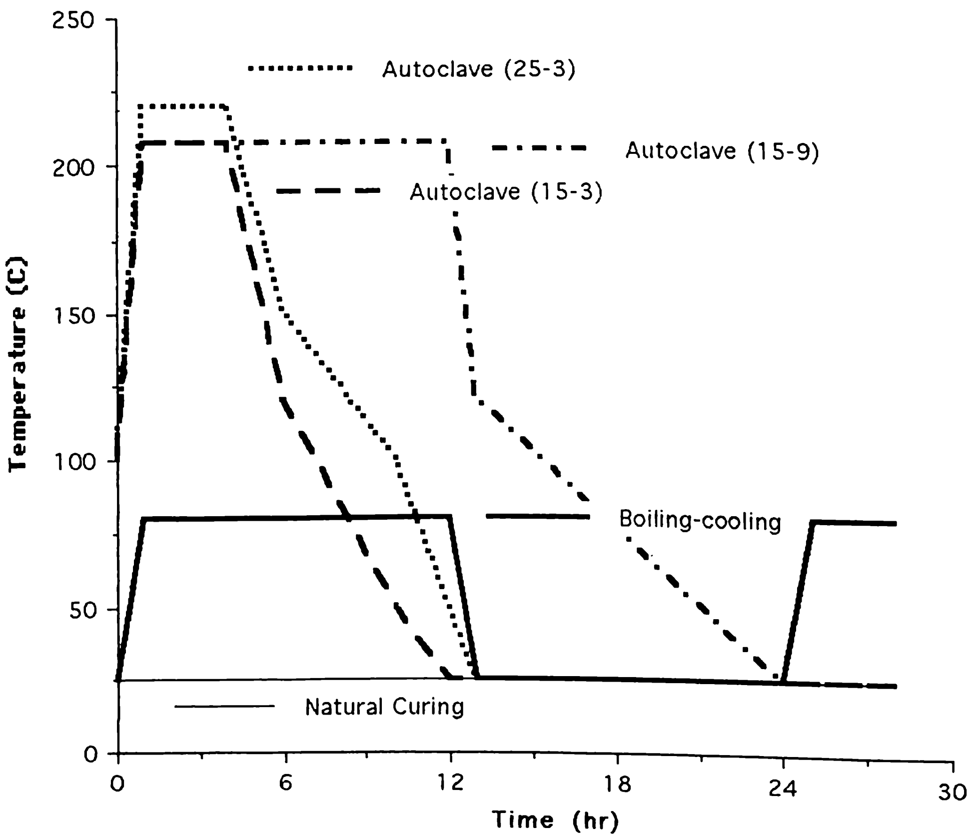

Figure 1
Temperature History of Various Curing Method

Boiling-cooling method of curing constitutes a cycle of 12 hours water bath curing at temperature of 80-90°C and a 12 hours of 25°C water curing, see temperature history in Figure 1. Strength of mortar specimens were evaluated at boiling cycles of 5, 10, 20 and 30 cycles. After a corresponding age or accelerated curing or cycle, the specimens 50x50x50 cubes specimen or 50 ϕ x 100 cylinders were tested in compression per ASTM C-311 and C-441, respectively.

Dimension Stability

Dimension stability and shrinkage properties were evaluated from a 25x25x280 mm specimens by 60 mm electrical resistant strain gages connected to the data logger (TDS 301) for 30 days. The shrinkage specimens were tightly sealed by plastic cover 24 hours after mixing in order to induce an autogenous shrinkage, that is, shrinkage in the absence of moisture from outside environment. The specimens were then stored at constant room temperature of $28^{o}C$.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Pozzolanic Materials

Test results show that the Pinatubo ejecta is a highly siliceous material rich in aluminum, calcium and sodium which is a typical characteristic of a natural pozzolan (Table 3). These oxide properties are of the same range as that observed by other researchers (Micosa et al., 1992; Bernardo, 1994). The SiO_2 of the Pinatubo pozzolan appears to be of relatively large percentage (i.e., 60-65%), which is a good preliminary index of the potential activity of a material to lime or cement binder. Chemical characterization of the Pinatubo pozzolan shows that the $SiO_2{:}Al_2O_3$ ratio ranges from 3.1 to 3.8, and the $SiO_2+Al_2O_3+Fe_2O_3$ composition ranges from 83 to 88% which is well above the chemical requirement set by the ASTM C-618 specification for the natural pozzolans. However, optional chemical requirement (ASTM C-618) of 1.5% minimum for the Na_2O component are not met because the average Na_2O composition of the pozzolans are in the vicinity of 4%. Hence, it is really necessary to evaluate the possible alkaline-aggregate reaction for this type of pozzolan. The result of this study, however, will be presented later in a separate publication.

X-ray diffraction results show that in spite of notable crystalline phases in the form of feldspar and amphiboles in various lahar samples, the presence of clear diffused band in almost all samples in the range of 20^{o} to 30^{o} is notably evident. It is also surprising to see that XRD of pozzolan samples from slurry sediment (S1) and pumicite stones (P1) of debris flow show a highly amorphous silica characteristic, as evident from the relatively less crystalline peaks (Figure 2). Generally, all the samples showed good potentials as a pozzolanic material, and this was confirmed from the ASTM C-311 standard of testing for pozzolanicity of a mineral sample.

Pozzolanic activity index test (ASTM C-311) with cement showed that Pinatubo ejecta in the form of slurry sediment (S1, S2) and the pumicite stones (P2,P3) have the highest silica reactivity of range of 89-97% comparable to 118% of Bataan fly-ash. These values are well above the 75% limit set by the ASTM C-618 specification for natural pozzolan. It is again confirmed in this experiment that the pozzolanic activity index of various type and source of ejecta are widely varied, and indeed there is a need for a faster evaluation of the activity index besides the ASTM C-311 test requirement of 28 days sealed curing. The results of the evaluation of the pozzolanic activity of various pozzolan under different types of accelerated curing are explained in detail in succeeding sections.

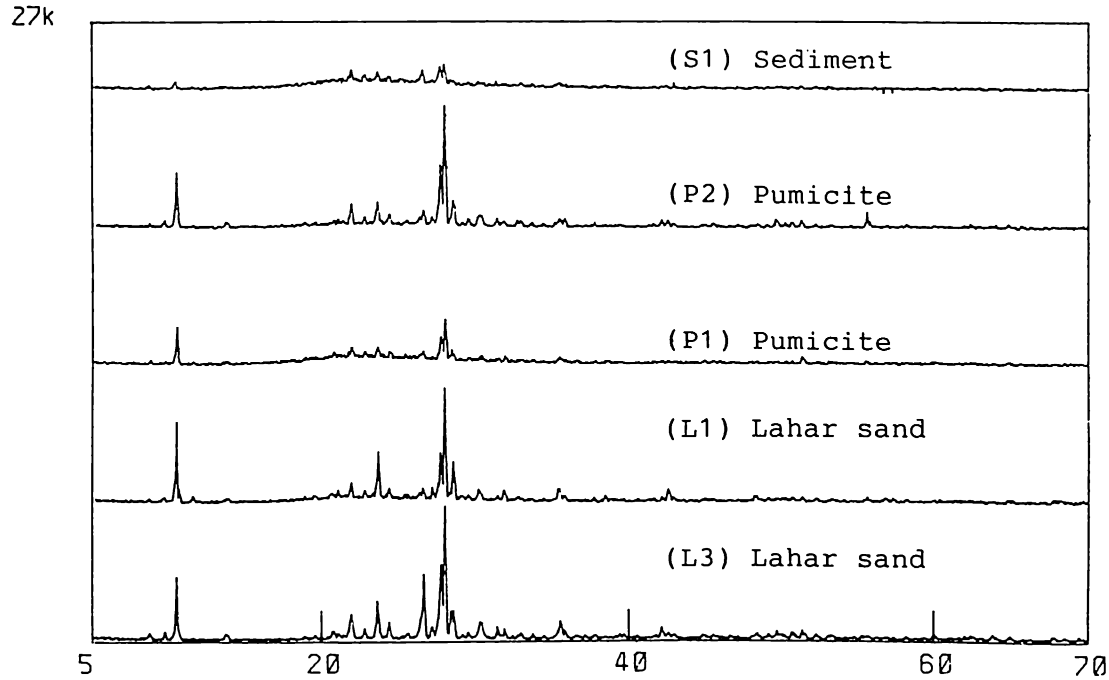

Figure 2
Typical X-ray Diffraction Results of Pinatubo Pozzolans

Response Under Natural Curing Condition

Table 4 summarizes the strength properties of various types of pozzolan at various percentage of cement replacement and various method of curing. It was observed that in spite of the varied 28-day strength for the 8 types of lahar material, generally the strength of blended cement mortar with pozzolanic addition of up to 20% possessed strength 10-30% higher than that of OPC (ordinary Portland cement) mortar. Increase in strength of cement-pozzolan mortar system are known to be induced by physical and chemical interaction of the constituents (Malhotra, 1992). Physical effect of space filling and chemical contribution to the formation of *CSHI* and *CSHII* or ettringite or related sulphoaluminate substances are the important factors in this strength development phenomenon.

It appears that mortar with pozzolan from the sediment of lahar slurry (S1,S2 series) showed the greatest strength improvement, followed by the lahar sand (L1, L2, L3 series), and lastly by the pumicite stones (P1, P2, P3 series). This behavior may be attributed to the greater fineness of pozzolan S1 and S2 and the amorphousness of its silica as observed from the XRD analysis. Furthermore it can be noted, that even though the Pinatubo debris material came from one source, the reactivity of different samples are widely varied. The authors believe that this may be attributed to the following reasons:

1. Reactive glass originated from various explosive eruptions have varying thermal history and different cooling process. This greatly influences the degree of reactivity of the

ejecta materials, in a sense that, during explosion that fused magma are pulverized by liberated gasses, and in this state the ejecta undergoes abrupt cooling which in turn prevents crystallization (Turriziano, 1980). Hence, varied thermal history can be considered as one of the major factors which affected the degree of silica reactivity of various samples.

2. Hyperconcentrated flow and debris flow of ejecta material from the volcano allowed the separation of minerals according to size, density and crystal type. Works of Hara (1994) showed that separation of minerals of Shirasu volcanic ash is possible through water elutriation, and it is possible to separate the glassy part with the crystalline part of the ash. As for the Pinatubo ash, the lahar flow must have induced the separation of minerals according to its fineness, density, and crystal type, thereby causing the varied pozzolanicity of various lahar materials.

Figure 3(a) to 3(c) show the effect of percent pozzolan replacement to cement for Pinatubo pozzolan (P3, L3) and fly-ash (FA) at 7, 28 and 63 days age respectively. It can be observed that both P3 and L3 series showed very little or no pozzolanic reaction at 7 days age. However, for the Calaca Bataan fly-ash, early pozzolanic reaction can be seen even for 30% replacement, indicating a highly reactive pozzolan. For cement replacement greater than 30%, it can be expected that a marked decrease in strength of as much as 50% will occur at the age of 7 days. This observed trend of slow strength development is a typical characteristic for general pozzolanic materials (Neville, 1981).

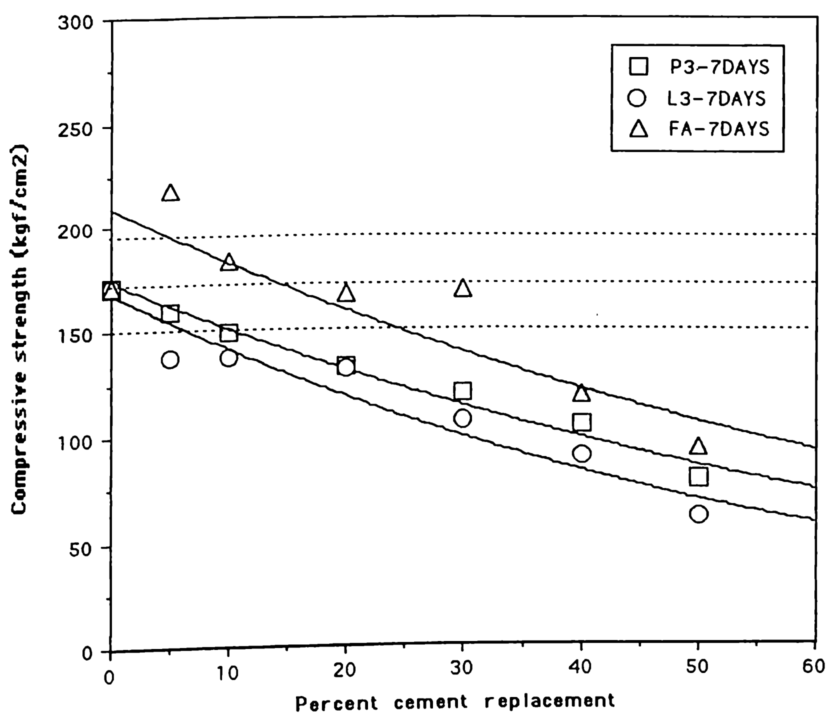

Figure 3(a)
Effect of Percent Pozzolan to 7 Days Compressive Strength

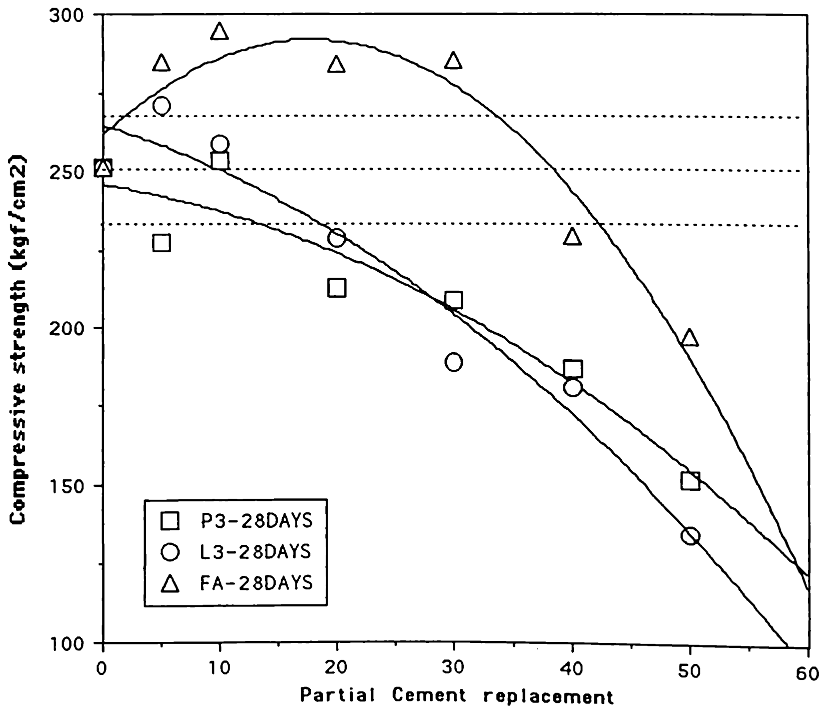

Figure 3(b)
Effect of Pozzolan to 28 Days Compressive Strength

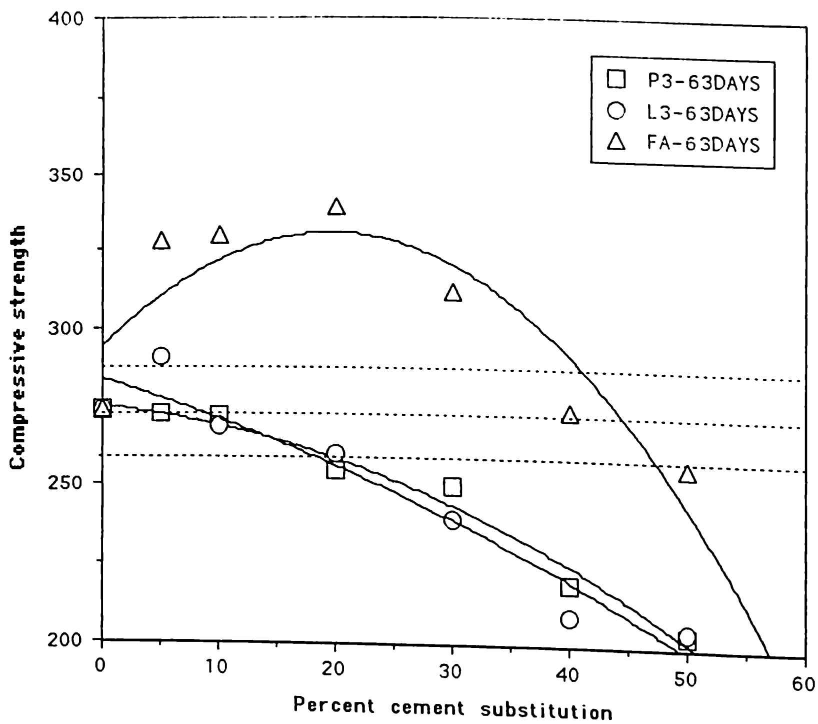

Figure 3(c)
Effect of Pozzolan to 63 Days Strength

At 28 days, the P3 and L3 pozzolan at 5, 10, and 20% replacement showed strength at the range of plain OPC mortar. Fly-ash on the other hand, showed a strength 12-18% higher than the control for cement replacement of up to 30%. Optimum proportion for the Pinatubo pozzolans are quite difficult to judge at 28 days, however, at 63 days it can be seen that 30% cement replacement will produce strength at par with plain cement mortar.

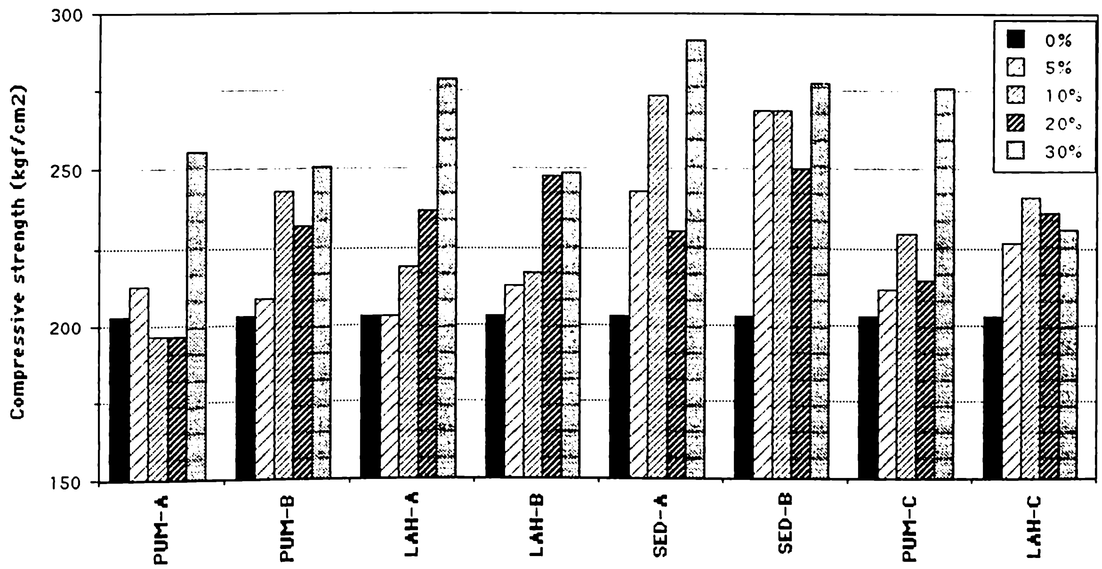

Figure 4
Effect of Type and Percentage of Lahar to the Compressive Strength of Autoclaved Mortar (15 kgf/cm^2 - 3 hours)

Response Under High Pressure Steam (Autoclave) Curing

Accelerated strength test such as autoclaving can be considered as a test in its own right and not merely as a means of predicting later age strength of concrete. From this base, accelerated method of curing can offer a more convenient and realistic way of ascertaining if the concrete will satisfy the purpose for which it was designed (Neville, 1981). It is in this context, that the need is warranted for an accelerated evaluation technique for the determination of the suitability of lahar material as an active addition to concrete. Theoretically, the rate of progress of the hydration of cement and the resulting strength gain is controlled by the temperature, humidity, and pressure during curing, therefore, high pressure steam and boiling-cooling process were adopted as medium for these accelerated curing technique.

From Figure 4 it is clearly evident that the compressive strength of all Pinatubo pozzolan for cement replacement of up to 30% increased remarkably, indicating the favorable condition of high pressure and high temperature for the reaction of SiO_2 of the pozzolan and the

$Ca(OH)_2$ liberated by the C_3S of cement. Neville (1981) also reported that high pressure steam curing is very effective for finely ground silica owing to the accelerated silica reaction. From among the 8 types of Pinatubo pozzolan, again the slurry sediment type (S1, S2) and the lahar sands (L1, L2, L3) appear to be the most reactive under this method of curing. Cement replacement of up to 30% seems favorable and gives high strength results. An average increase of 18-25% can be expected for 30% replacement, while and average of 10-15% for 5, 10 and 20% replacement. The difference in the strength increase observed for various percent of pozzolan can be attributed to the total available amount of silica reacting with the $Ca(OH)_2$ of cement, i.e., the greater SiO_2 reacting with lime the higher the strength. Furthermore, the ability of cement mortar to gain higher strength under high pressure steam curing is also dependent on C_3S/C_2S ratio, i.e., moderately low C_3S/C_2S ratio gives better strength results (Neville 1981). Substitution of pozzolan to cement ultimately reduces the overall C_3S/C_2S ratio, making it very favorable for autoclaving condition.

It can be observed that strength level of pozzolan-cement mortar with 5% up to 50% cement replacement is either of the same range or significantly higher than the plain OPC mortar. This indicates that silica reaction is still effective even for very large percent of cement replacement. Optimum proportion of cement and Pinatubo pozzolan under autoclave method of curing appears to be 60:40, that is, a replacement of cement by lahar to as high as 40% (cf.Figure 5). The lower optimum value of 30% observed from the natural curing method may be caused by incomplete silica reaction with cement, whereas the autoclaving condition speeded-up the reaction with the aid of high temperature.

Figure 5-6 show the response of the three pozzolan (L3, P3, FA) at various autoclaving condition. It can be seen that for pressure of 15 kgf/cm^2, the most favorable retention time based on the criteria of strength and economy appears to be at 3 hours, because increase in strength is minimal for retention time of 6 and 9 hours. The same observation was seen by Hara (1994) when he tested autoclave compact with silica sand, fly-ash and Shirasu volcanic ash as mineral admixture under 15 kgf/cm^2 pressure and retention time of 4, 8 and 16 hours. His findings also revealed that there are very little or no increase in strength of autoclave specimens retained in chamber for 4 or 8 hours. The author presumes that at microstructure level, reaction of silica with $Ca(OH)_2$ starts as interfacial surface reaction which later progresses inward depending on the moisture and external environment. This phenomenon was observed at some extent in a hydrating cement particle (Willimason, 1990), fly-ash reacting with $Ca(OH)_2$ (Malhotra, 1993) and cement particle with glass aggregates (Barnes et al., 1978). It is possible that the first couple of hours of steam curing constitute this surface reaction. The rate of reaction and the production of hydration products at the time stage greater than 3 hours may be relatively of lesser degree compared to the first couple of hours. However, it should be noted that the comparison of the effect of retention time in this study is between 3, 6 and 9 hours only and does not cover the time in excess of 9 hours. Thus, for retention time of up to 9 hours, the effect to strength can be considered to be not very significant.

Hence from these test results, silica reactivity and latent hydraulicity of both Pinatubo pozzolan and the Bataan fly-ash can be sufficiently enhanced by elevated high pressure steam curing of 15 kgf/cm^2 for 3 hours. Autoclaving method can therefore be used as an accelerated curing technique in the determination of the degree of pozzolanicity of lahar material and also in the determination of the optimum proportioning of ejecta with Portland cement.

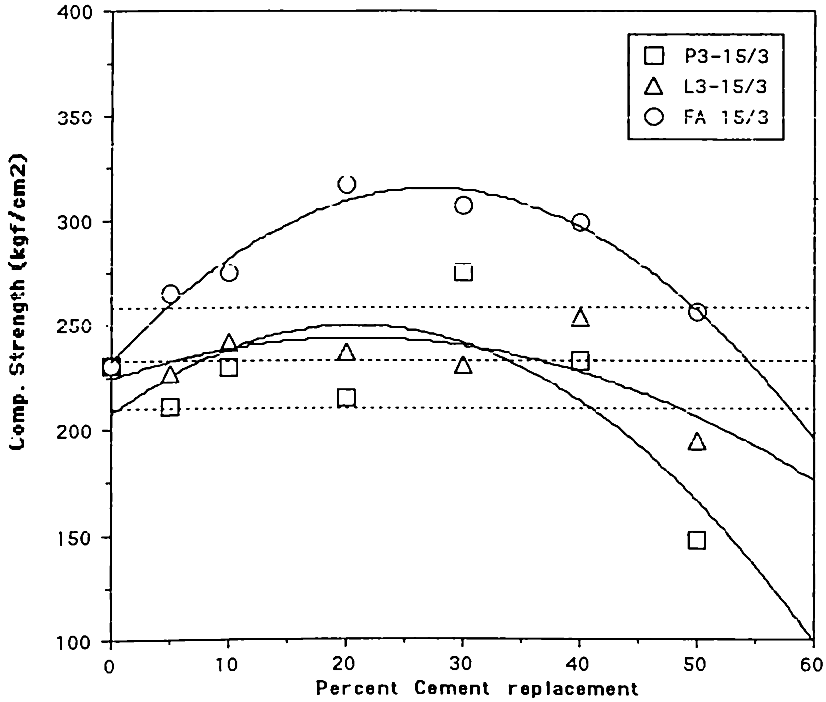

Figure 5(a)

Optimum Percentage Substitution of Pozzolan to Mortar under Autoclaving (15 kgf/cm^2 - 3 hours)

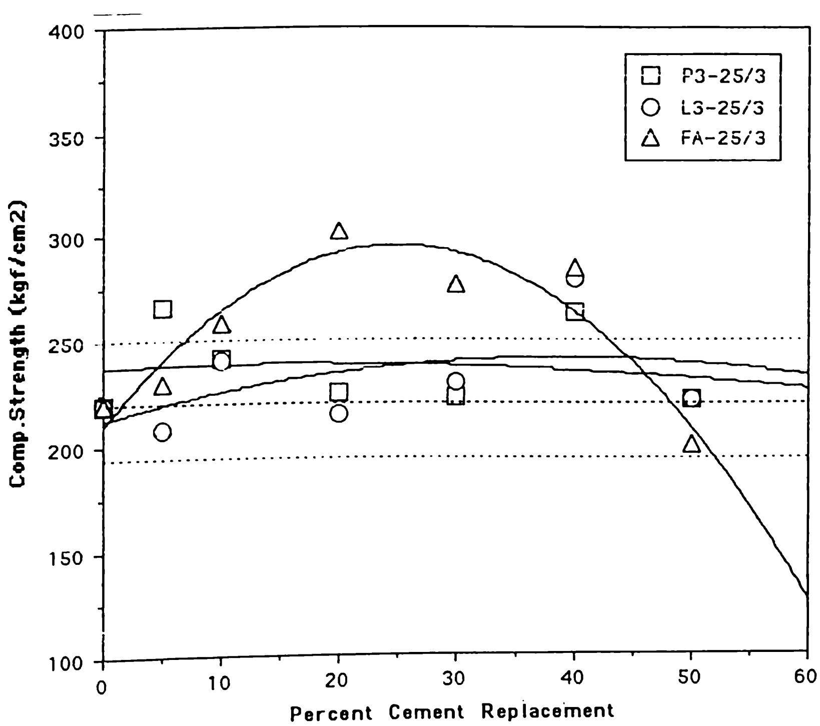

Figure 5(b)

Effect of Pozzolan to Autoclave Strength (25 kgf/cm^2 - 3 hours)

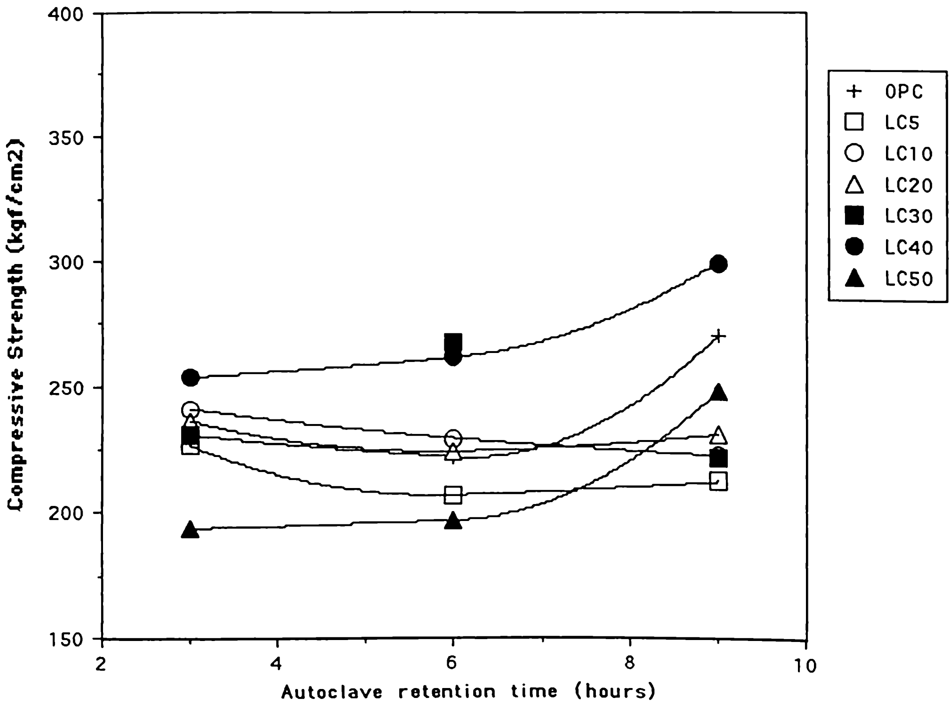

Figure 6(a)
Effect of Autoclave Retention Time to Strength (L3 series)

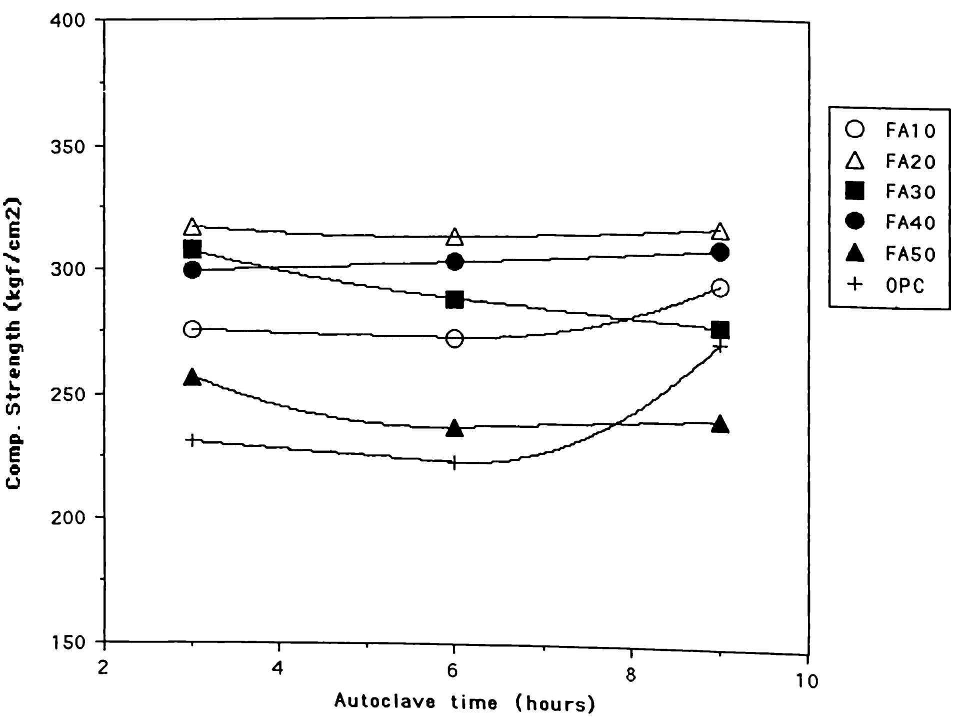

Figure 6(b)
Effect of Autoclave Retention Time to Strength (FA series)

Response Under Boiling-Cooling Method of Accelerated Curing

The ASTM C-684 employs the boiling method to determine the projected 28 days strength of concrete based on a 48 hours strength. The boiling method adopted in this study, however, is quite different, because the 24-hour aged specimen is immersed in a water bath with temperatures of 80-90^{o}c for the 12 hours followed by 12 hours cooling in water, and strengths were determined after 5, 10, 20 and 30 cycles. The US Corps of Engineers adopted this same accelerated curing for control purposes and prediction of strength at later age. Their results showed that this method is a good indicator of a 1-year strength of concrete specimen (Grant 1977; Neville, 1981).

It was observed that at 5 cycles of boiling the P3 and L3 series showed no decrease in strength up to 30% percent replacement, as a matter of fact an increase in strength of as much as 6-10% was seen, indicating an early silica reaction (Figures 7(a)-7(b)). The 5 cycles boiling regime actually took 7 days to complete, and if this 5 cycles is compared to the strength at 7-day natural aging, it can be seen that a marked increase in strength of as much as 50% occurred for all percentage replacement. This actually indicates an early silica reaction which took place in the cement system.

Higher boiling cycles confirmed the observed 30% replacement as the optimum percentage replacement of Pinatubo pozzolan. Although at 10 and 20 boiling cycles, strength level equal with the OPC mortar were achieved even up to 40% replacement, indicating the presence of latent reactivity and hydraulicity at this high range of substitution (cf. Figure 8). Hence, from the boiling cycle method of curing, it can be recommended that it is possible to determine the latent reactivity and hydraulicity of a given pozzolan by a 5 cycle boiling method of curing which is approximately a 7 days test.

Dimension Stability

It is well recognized that the fineness of cement, the aggregate particles, the mixture proportions are few of many internal factors which affect the shrinkage properties of the matrix system. For a matrix system with constant water content, aggregate type and content under laboratory condition, the fineness of the cement and the resulting properties of the hydration products are the factors which can greatly affect the shrinkage properties. The influence of different types and proportion of pozzolan on the shrinkage properties are shown in Figures 9(a)-9(b). The origin of the shrinkage strain and age graphs in these figures refers to the time when setting and reading the electrical resistance strain gages measurement, started which is approximately 24 hours after mixing. It can be observed that the 10%, 20%, and 30% pozzolan showed shrinkage 13-25% higher than the plain OPC mortar. On the other hand, 40 and 50% pozzolan showed initial expansion for the first 48 hours at about $50x10^{-6}$ to $150x10^{-6}$ mm/mm which resulted to an overall decrease in the shrinkage of the specimen. Different shrinkage response of various cement-pozzolan blend mortar may be attributed to either physico-chemical or mechanical restraint factors inside the system. This observed trends are believed to be caused by the following factors

1. Increasing the percentage volume of pozzolan which is relatively coarser in fineness (low

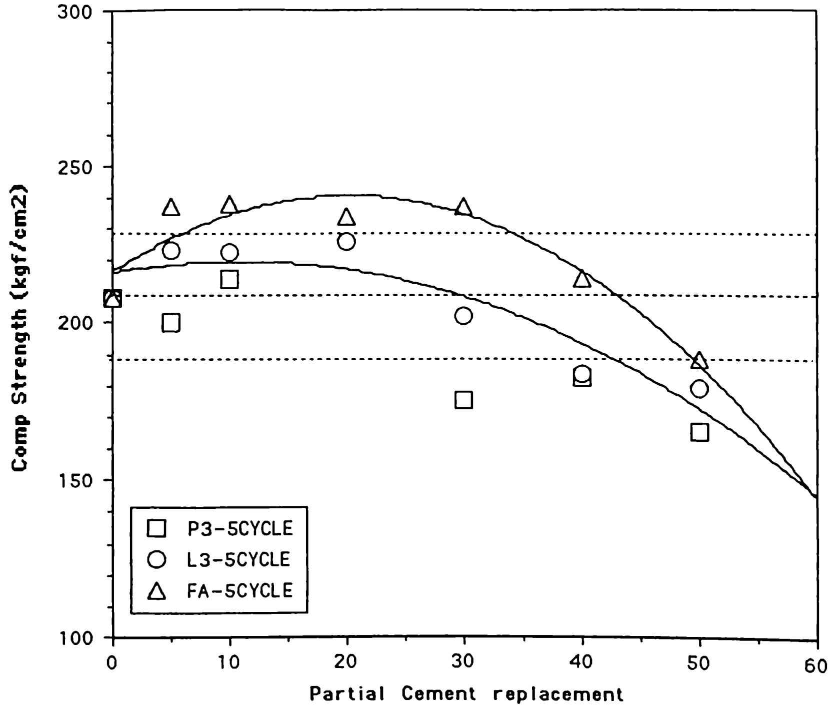

Figure 7(a)

Effect of % Pozzolan to Mortar Strength under 5 Cycles of Boiling

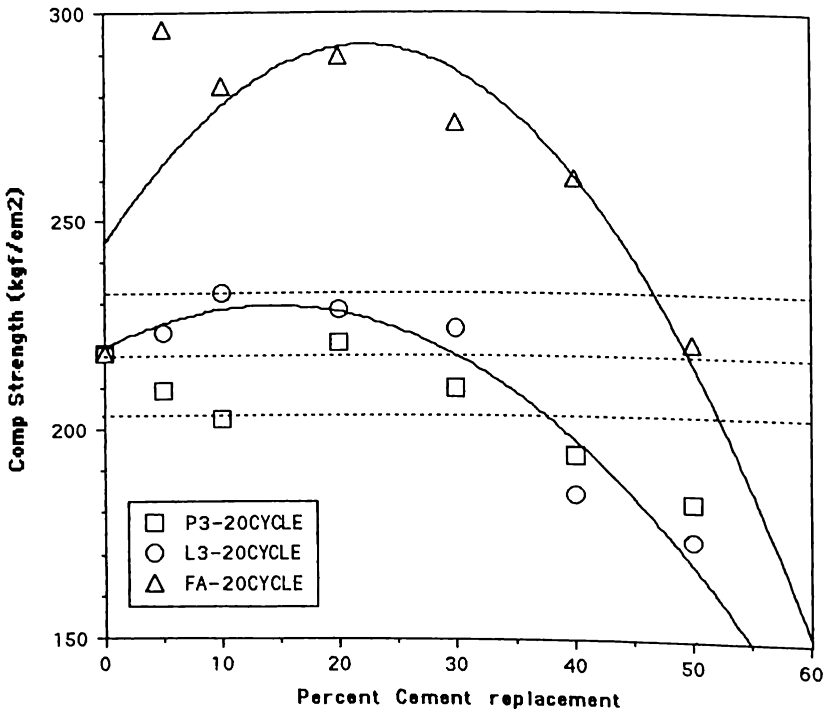

Figure 7(b)

Effect of % Pozzolan to Mortar Strength under 20 Cycles of Boiling

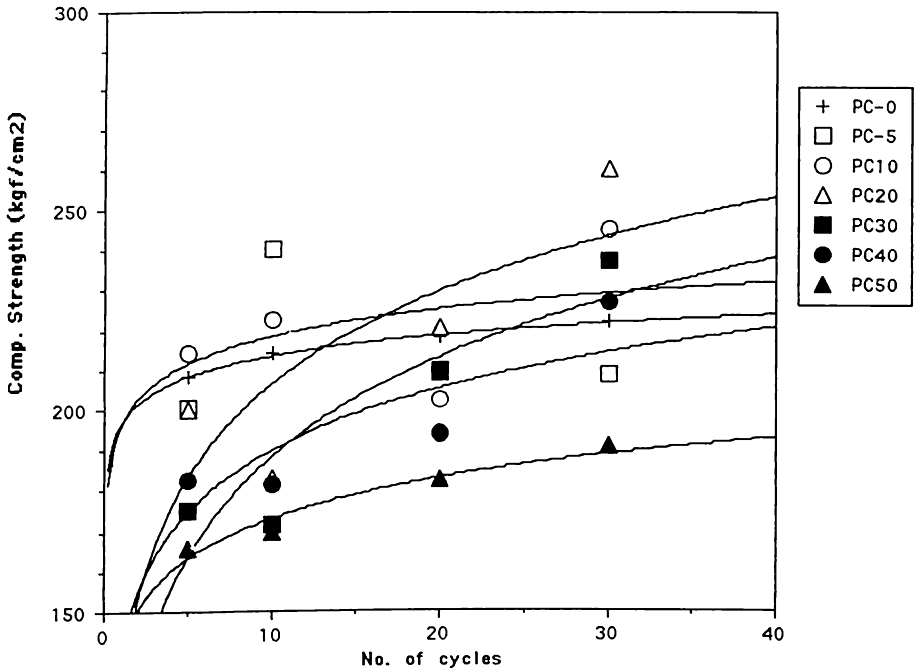

Figure 8(a)
Effect of Accelerated Curing (Boiling Method) to the Strength Development of Mortar with P3 Pozzolan

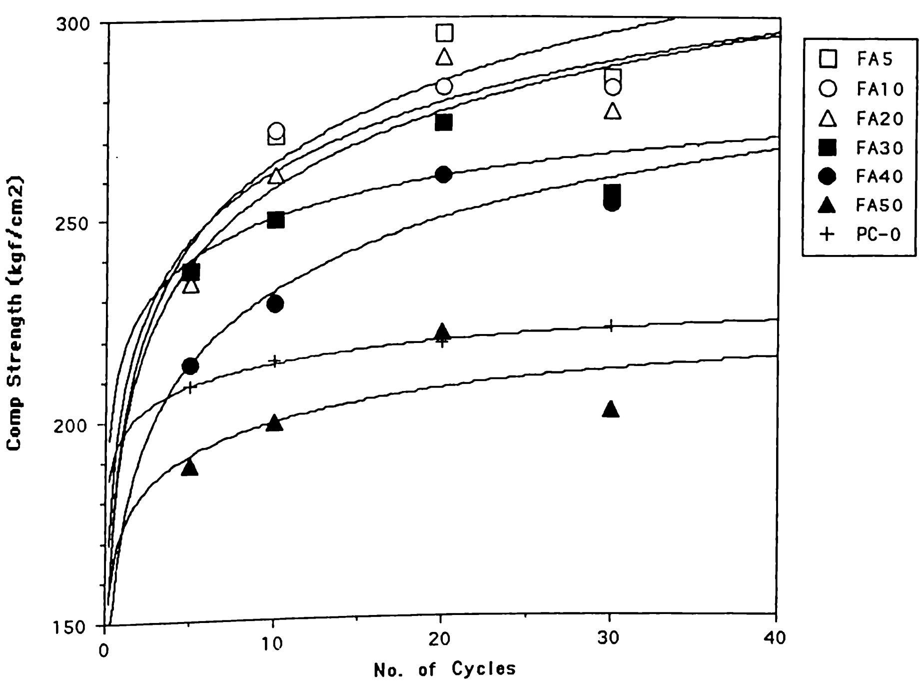

Figure 8(b)
Effect of Accelerated Curing (Boiling Method) to the Compressive Strength Development of Mortar with Fly-ash

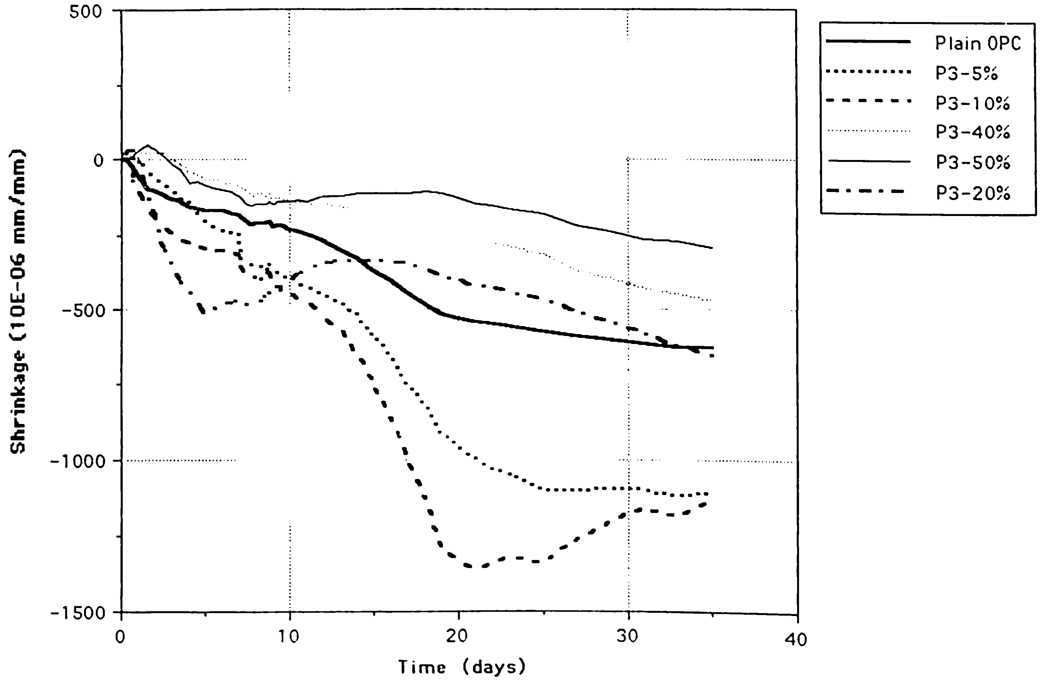

Figure 9(a)
Effect of % Replacement of Pinatubo Pozzolan (P3 series) to Shrinkage Properties of Mortar

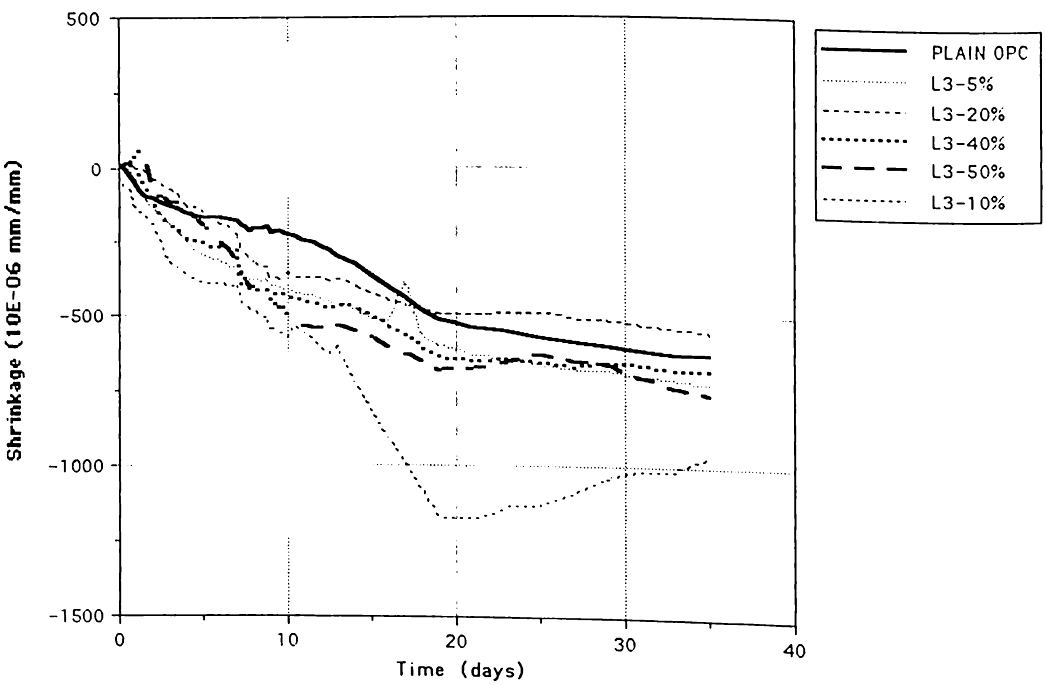

Figure 9(b)
Effect of % Replacement of Pinatubo Pozzolan (L3 series) to the Shrinkage Properties of Mortar

specific surface) compared to cement, and also which hydrates comparatively less may have offered restraining effect to the shrinkage of the cement matrix system.

2. Various percentage of cement replacement by pozzolan consequently alter the overall chemical composition (e.g., C_3S/C_2S ratio, alkali content) of the cementitious material which can result to a varying changes in strength development and ultimately in shrinkage or expansion properties. For example, Neville (1981) noted that a few percent increase in the alkali of the matrix may result to lower strength gain (i.e., less stiffness) and relatively higher drying shrinkage. Chemical analysis results of pozzolans already revealed high alkali content of about 4% and which may have contributed to greater shrinkage observed for 10 and 20% substitution and apparent expansion for the 40 and 50% pozzolan.

3. Various cement replacement by pozzolan ultimately changed the resulting porosity of the matrix system at varying degrees which in turn affects the degree of in-out movement of pore water and free water in the system. It is well known that the mechanism of dimension stability especially drying shrinkage of a concrete material is directly related to the withdrawal of water from its system, and it is postulated that shrinkage is also related to the removal of zeolitic water in the matrix system.

Hence, alteration of the physical and chemical properties of the cement system may be considered as the prime cause of the variation of the shrinkage properties.

CONCLUSION

This development research has shown that the Mt. Pinatubo ejecta is a highly feasible pozzolanic material for active addition to cement in construction, cement and concrete industries. Utilization of this abundant volcanic ejecta will ultimately solved two significant problems, namely, elimination of ill-wanted materials and provision for a valuable construction material. Based from experimental results, the following significant conclusions can be drawn:

1. Pinatubo ejecta is a highly siliceous material rich in aluminum, calcium and sodium with varied pozzolanicity. From the basis of test results of eight types of Pinatubo pozzolans, it was found that the pozzolanic activity index varied from 82-97%, and the physical and chemical properties as set by the ASTM C-618 specification for natural pozzolans are satisfactorily met.

2. From the strength development data, it seems that during the first 7 days of hydration pozzolanic reaction did not make any contribution to the strength of blended Pinatubo pozzolan-cement mortar. During the 28 to 63 days period, however, pozzolanic activity was very significant because mortar containing up to 30% pozzolan showed strength equal or significantly higher than the control OPC mortar especially at 63 days period. Optimum replacement of lahar to Portland cement was found to be at 30%.

3. Application of hydrothermal reaction such as high pressure steam curing (autoclave) can enhanced the reactivity and latent hydraulicity of Pinatubo pozzolan. Optimum

proportions of cement and pozzolan appears to be at 60:40 ratio, and the optimum autoclaving condition was found to be 3 hours retention time under a pressure of 15 kgf/cm^2. Potential pozzolanic activity of any given lahar material can be adequately evaluated by the autoclaving method similar to the ASTM C-151 execution.

4. Boiling-Cooling cycle method of accelerated curing can be used to determine the potential activity or latent reactivity and hydraulicity of any given lahar material. The 5 cycle boiling method was found to be sufficient to predict the pozzolanic reactivity and probable optimum proportion of pozzolan and cement. Optimum proportion of 30% observed from both 28 days natural curing and accelerated autoclaving method were confirmed in the boiling method of curing.

5. The drying shrinkage values of the blended pozzolan cement mortar were found to be essentially similar. 5, 10 and 20% pozzolan showed a slight increase of 13-25% in shrinkage, while a 40 and 50% pozzolan showed a decrease of 5-10% in the drying shrinkage.

ACKNOWLEDGMENT

The authors wish to express their gratitude to Mr. Rogelio Irabon for his assistance in the preparation and testing of specimens. Special thanks are due to Prof. Goro Shimizu of Nihon University for providing the X-ray diffraction analysis of Pinatubo samples, and to Dr. Zingapan for providing the fly-ash from Bataan NPC Coal plant. Thanks is also due to the rest of the staff of the Civil Engineering Department of the Integrated Research and Training Center (IRTC-TUP) for their comments during the experimental stage of this project.

REFERENCES

Acda, M. and Gibe, A. (1992). Volcanic ash as grain protectant of palay and corn. Abstracts of International Scientific Conference on Mt. Pinatubo, May 1992, DFA Philippines, pp. 21.

Alabastro, E. (1994). Private Communication to Executive Director of IRTC-TUP, DOST-PCIERD, Philippines.

Almeniana, Q. F.(1993). Analysis of grain fineness of ashfall emitted by Mt. Pinatubo as substitute molding sand for foundry. Proceedings of 3rd IRTC Civil Engineering International Conference, March 1993, IRTC Press, Philippines, pp. 283-290.

ASTM (1993). Concrete and Mineral Aggregates. Annual Book of ASTM Standards vol.04.02, ASTM Philadelphia, pp. 889.

ASTM (1993). Cement; Lime; Gypsum. Annual Book of ASTM Standards vol.04.02, ASTM Philadelphia, pp. 679.

Barnes, B.D., Diamond, S. and Dolch, W.L. (1978). The contact zone between Portland cement paste and glass aggregate surface. Cement and Concrete Research, vol.8, pp. 233-244.

Bernardo, S.T. (1994). Characterization and some practical uses of Pinatubo pyroclastic fall deposits. International Symposium on Utilization Technology of Volcanic Ejecta, March 1994, Agency of Industrial Science and Technology (ITIT), Japan, pp. 75-84.

Delos Reyes, P. (1994). Pinatubo Volcano and its eruptive products. International Symposium on Utilization Technology of Volcanic Ejecta, March 1994, Agency of Industrial Science and Technology(ITIT), Japan, pp. 12-24.

Diamond, S. (1983). On the glass present in low calcium and in high calcium fly-ash. Cement and Concrete Research, vol.13, pp. 459-464.

Espina, C. and Oana, J. (1994). The challenges and potential on the Utilization of the Mt. Pinatubo ejecta: A general assessment of studies undertaken by selected agencies in the Philippines. International Symposium on Utilization Technology of Volcanic Ejecta, March 1994, Agency of Industrial Science and Technology (ITIT), Japan.

Grantt, N.T. and Warren, P.A. (1977). Forecasting concrete strength. Civil Engineering, July-August 1977, pp.201-209.

Hara, N. (1994). Utilization of Volcanic ejecta for building materials. International Symposium on Utilization Technology of Volcanic Ejecta, March 1994, Agency of Industrial Science and Technology (ITIT), Japan.

Ignacio, U. et.al.(1994). A study on the Appropriate Design mix of portland cement/Pinatubo lahar material for pre-fabricated structural component and Pavement blocks; and Pinatubo lahar material/clay for soil erosion control structures. Final report submitted to DOST-PCIERD, Aug. 1994, UP-BRS, Philippines.

James, J. and Rao, M.S. (1986). Reaction product of lime and silica from rice husk ash. Cement and Concrete Research, vol.16, pp.67-73.

Malhotra, V.M. (1992). CANMET Investigations dealing with high volume fly-ash concrete. Advances in Concrete Technology (ed. V.M. Malhotra) Canada Communication Group. pp. 433-470.

Malhotra, V.M., Carette, G.G. and Bremner, T.W. (1993). Performance of high volume fly-ash concrete at a marine exposure at Treat island, Maine. Proceedings of Durability of Building Materials and Components, vol.2, E & FN Spon, Tokyo, pp. 1011-1020.

Mendoza, T.C. and Cabangbang, R.P (1992). Effects of Mt. Pinatubo eruption in crop production systems. Abstracts of International Scientific Conference on Mt. Pinatubo, May 1992, DFA Philippines, pp. 17.

Metra, T.M., De dios, J.L., Sta. Cruz, P.C. and Corpuz, A.A. (1992). Effect of fertilizer application in lowland rice varieties planted in volcanic ash laden soils. Abstracts of International Scientific conference on Mt. Pinatubo, May 1992, DFA Philippines, pp.18.

Mehta, P.K. (1981). Studies on blended Portland cement containing santorin earth. Cement and Concrete Research, vol.11, pp. 507-518.

Micosa, A.G., Carating, R.B. and Tokudome, S. (1992). Extent and some properties of Mt. Pinatubo's ashfall over agricultural lands. Abstracts of International Scientific Conference on Mt. Pinatubo, May 1992, DFA Philippines, p.16.

Neville, A. (1981). Properties of Concrete 3rd Edition, Pitman Press U.K., pp. 777.

Pagbilao, D. and Agron, J. (1993). Paving block design mix Report. ITRC-TUP Internal Report, ITRC Press.

Price, W.H. (1975). Pozzolans-A Review. ACI Materials Journal, May 1975, ACI-USA, pp. 225.

Shimizu, G. and Jorillo, P. (1992). Use of Mt. Pinatubo for Materials for Construction. Abstracts of International Scientific Conference on Mt. Pinatubo, May 1992, DFA Philippines, pp. 21.

Shimizu, G. and Jorillo, P. (1993). Investigation of volcanic ash from Mt. Pinatubo as a construction material. Proceedings of 3rd IRTC Civil Engineering International Conference, March 1993, IRTC Press, Philippines, pp. 223-235.

Talero, R. (1990). Qualitative analysis of natural pozzolanas, fly-ashes, and blast furnace slags by XRD. Journal of Materials in Civil Engineering, ASCE vol.2, no.2, May 1990, pp. 106-115.

Turriziani, R. (1980). Aspects of Chemistry of Pozzolanas. Chemistry of Cement, vol.2 (ed. Lea, R.M.).

Williamson, R.B. (1990). Solidification of Portland Cement. Progress in Material Science.