

## Pozzolan characteristics of Young Toba Tuff

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**Portland Pozzolana Cement (PPC) is widely used to achieve durable and sustainable concrete in modern construction. In the present study, the potential use of natural volcanic ash in the manufacturing of PPC has been studied. Young Toba Tuff (YTT) was collected from Jwalapuram, Andhra Pradesh, India. The pozzolan performance of this ash was assessed by Strength Activity Index (SAI) and Frattini test. SAI of YTT was found to be above 75% for sufficient pozzolanicity. Further, the results of Frattini test were below the lime solubility curve, indicating that YTT could be potentially useful as pozzolan material in concrete.**

**Keywords:** Concrete, pozzolan characteristics, strength activity index, volcanic ash.

YOUNG TOBA TUFF (YTT) is a fine volcanic ash material during the late Quaternary period (74,000 years BP)<sup>1</sup>. The ash is formed due to bubble bursts in the expansion of upcoming gas in the magma<sup>2</sup>. YTT erupted due to the collision between the Indo-Australian plate and the Eurasian plate near the Lake Toba caldera, Indonesia<sup>3</sup>.

Cement is manufactured in more than 150 nations all over the world and India is the second largest producer<sup>4</sup>. More than 70% of the cement used in India is in a blended form, either as Portland Pozzolana Cement (PPC) or Portland slag cement. PPC is usually a blend of 10–30% pozzolan material (typically fly ash) with cement clinker, which reduces the carbon dioxide emitted per tonne of the product<sup>5</sup>. Materials having fine grain size, amorphous in nature with a glassy texture and rich in reactive silica are considered to be good pozzolan materials<sup>6–8</sup>. These materials react with the hydrated lime produced from cement hydration to produce additional calcium silicate hydrate<sup>9</sup>. In the past, calcined clay has been successfully used as a substitute for natural pozzolan material<sup>10</sup>.

The name ‘Pozzolana’ was derived from a place called Pozzuoli in Italy, where volcanic ash was utilized as a binding material with lime. Researchers from all over the world are interested in establishing YTT as a stratigraphic marker for the geological field of chronostratigraphy, palaeoenvironment and palaeoclimate<sup>11</sup>. A comprehensive study has been carried out on YTT ash by many

authors<sup>1,11–16</sup>, but the pozzolan evaluation of this material is not available in the existing literature. In this context, the YTT ash needs to be studied as pozzolan material.

Pozzolan characteristics of YTT material can be determined by strength activity index (SAI). In this test, cement mortar specimens (50 × 50 × 50 mm) are prepared with 20% replacement of cement by YTT and the compressive strength is compared with control specimens (i.e. of mortar without YTT). The pozzolan activity is represented as the strength of the pozzolan mortar as a percentage of the strength of the control mortar. Any material that results in >75% SAI is deemed to be pozzolan. In the case of Frattini test, the consumption of Ca<sup>2+</sup> and OH<sup>-</sup> is determined using direct chemical analysis. The present study aims to characterize YTT ash as a pozzolan and to evaluate its potential for use as a cement additive in the production of PPC.

YTT used in this study was collected from the Jwalapuram site situated along the banks of the Jurreru river, Andhra Pradesh, India (15°19'20.2"N; 73°08'00.1"E; elevation: 257 m amsl). A trench to a depth of 3.50 m was dug and the exposed litho section described in the field for its geological characteristics (Figure 1). Based on colour and sediment texture the exposed section was divided into four layers by marking the zero level at the line of contact between layer C (volcanic ash) and layer D (silty soil) (Figure 1). The thickness of volcanic ash deposit in the Jwalapuram trench is nearly 2.27 m and an overburden of sediment above the ash is ~1 m.

Volcanic ash is fine silty in nature and its mean grain size ranges between 15 to 63 µm (ref. 16). The bulk chemistry (silica versus alkaline) of volcanic ash was compared with ash from the study area<sup>15</sup> and the source of YTT<sup>13</sup> indicated as rhyolite magma<sup>17</sup> (Figure 2). The above result reveals that volcanic ash collected from the Jwalapuram site is similar to the YTT eruption in Indonesia<sup>12</sup>.

YTT samples collected from the Jwalapuram trench were sieved and passed through the #120 ASTM mesh (125 µm) for determining the grain size and were examined using different techniques. The particle size distribution was determined by laser diffraction method using a Malvern Mastersizer instrument at the Department of Geology, Anna University, Chennai. Physical properties such as specific gravity, Blaine’s air permeability, moisture content, loss on ignition, normal consistency and setting time were tested in accordance with IS: 1727–1967 (ref. 18). The chemical composition of the ash was determined using X-ray fluorescence spectroscopy (Bruker S4-Pioneer). Surface morphological characteristics were examined using a microscope Hitachi S-3400N and semi-quantitative analysis by X-Ray powder diffraction (XRD) (Bruker D2 Phazer diffractometer).

The cumulative particle size curve and distribution curve of YTT (Figure 3) shows the graphical mean size

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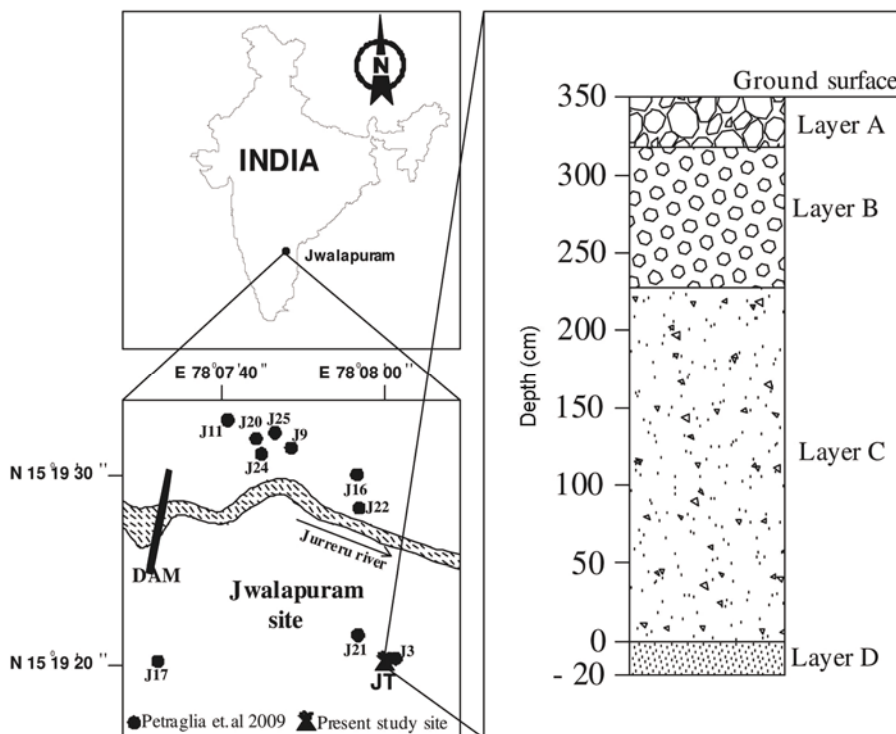


Figure 1. Location map and litho section of the Jwalapuram trench (JT).

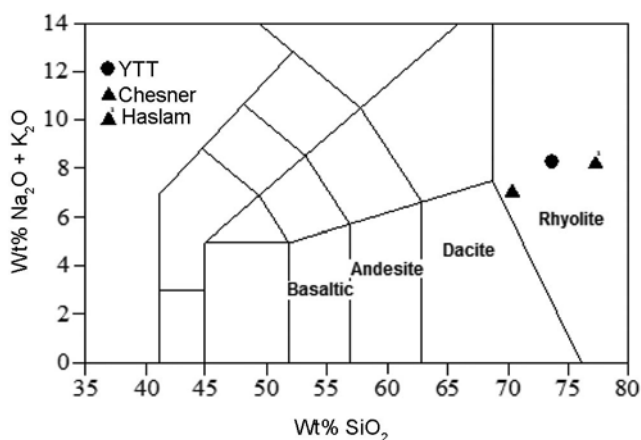


Figure 2. Young Toba Tuff (YTT) plotted on total alkalis versus silica diagram.

( $d_{50}$ ) to be 35.9  $\mu\text{m}$ . The distribution is also comparable to the commercial 53 grade Ordinary Portland Cement (OPC) chosen for this study.

The physical and chemical characteristics of YTT (Table 1), indicate that it has very low moisture content (1.03%), specific gravity (2.30) and specific surface area (164  $\text{m}^2/\text{kg}$ ). YTT is rich in  $\text{SiO}_2$  content (73.54 wt%), with low values of  $\text{Al}_2\text{O}_3$  (13.53 wt%),  $\text{Fe}_2\text{O}_3$  (1.49 wt%) and  $\text{CaO}$  (1.65 wt%). The physical performance, in terms of consistency and setting times according to IS 1727, is satisfactory.

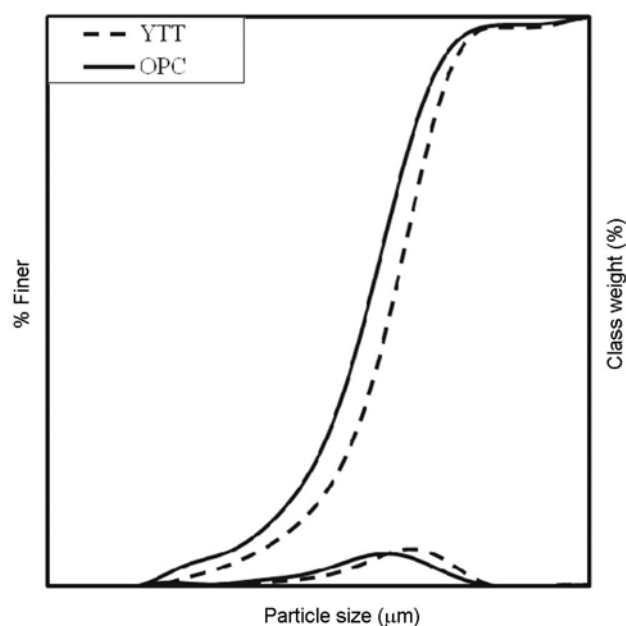


Figure 3. Cumulative and distribution curve of YTT and Ordinary Portland Cement (OPC) cement.

Chemical characteristics of YTT are similar to fly ash, as indicated by a comparison (Table 2) of its properties with the fly ash standard IS: 3812–1981 (ref. 19).

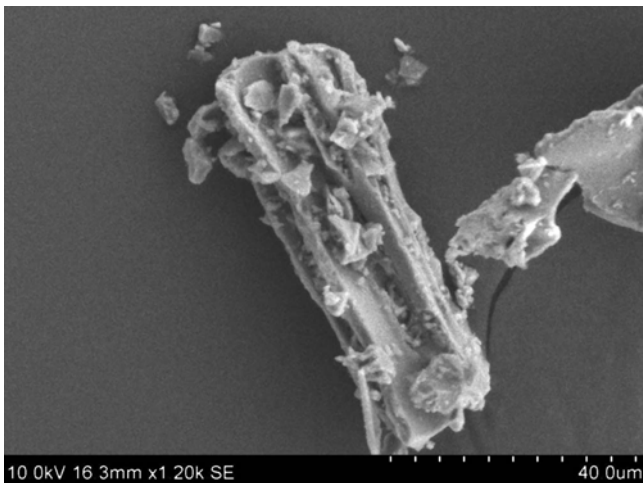
The surface morphology of YTT is elongated glass with double-walled bubbles (Figure 4). These morphological

**Table 1.** Physical and chemical characteristics of Young Toba Tuff (YTT)

Physical characteristics		Chemical characteristics	
Characteristics	YTT	Oxide	YTT (%)
Specific gravity	2.30	CaO	1.65
Specific surface area (Blaine's)	164 m <sup>2</sup> /kg	SiO <sub>2</sub>	73.54
Moisture content	1.03%	Al <sub>2</sub> O <sub>3</sub>	13.53
Loss on ignition	5.69%	Fe <sub>2</sub> O <sub>3</sub>	1.49
Normal consistency	32%	Na <sub>2</sub> O	4.19
Initial setting time	160 min	K <sub>2</sub> O	4.15
Final setting time	210 min	SO <sub>3</sub>	0.17

**Table 2.** Comparison in chemical specifications of YTT with IS: 3812-1981

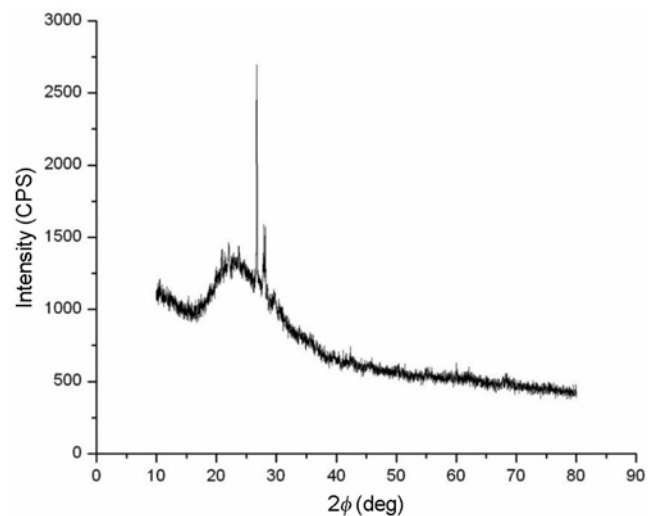
Requirement	IS: 3812-1981	YTT
SiO <sub>2</sub> + Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> %	Minimum 70	88.56
SiO <sub>2</sub> %	Minimum 35	73.54
MgO %	Maximum 5	0.53
SO <sub>3</sub> %	Maximum 2.75	0.17
LOI %	Maximum 12	5.69

**Figure 4.** Surface morphology of YTT as seen in secondary electron imaging.

features suggest that these glass shards are of magmatic origin. YTT is rich in amorphous silica and a clear amorphous hump in the XRD pattern is observed between 20° to 25° 2θ indicating occurrence of reactive silica (Figure 5).

Different standard tests are available to evaluate the pozzolanic activity of supplementary cementitious materials. The tests conducted in the present study to determine the pozzolanic characteristics are described below.

The SAI test was performed according to ASTM C311 (ref. 20). Three control mortar cubes of 5 cm size were prepared by mixing 500 g of OPC (53 grade), 1350 g of sand and 242 ml of water (0.484 w/c) in a planetary orbital mixer for 5 min. The cubes were demoulded after

**Figure 5.** XRD spectrum of YTT showing amorphous hump in the reactive silica region.

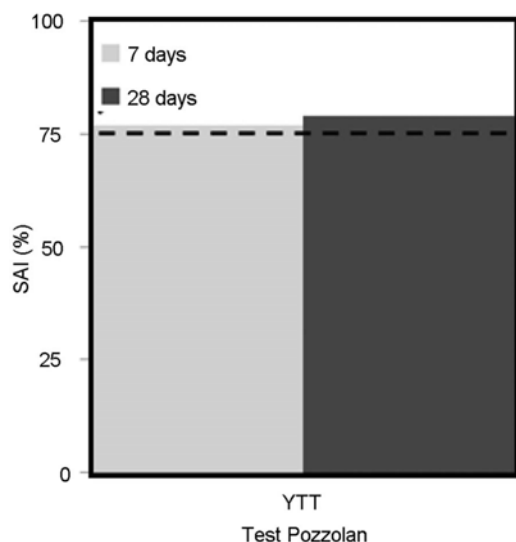
24 h, and then immersed in water saturated with lime at 25 ± 1°C until the testing age. Three specimens were tested in compression using a universal testing machine after 7 and 28 days. Similarly, the cubes for the replacement mortar were prepared with similar to control mortar. Three samples of 5 cm cubes with OPC 53 and 20% of YTT was used. The strength results reported here are the average of three tests, and SAI is presented as the percentage strength of YTT mortar relative to the control mortar, i.e.

$$\text{SAI (\%)} = \left( \frac{\text{Compressive strength of replacement mortar}}{\text{compressive strength of control mortar}} \right) \times 100.$$

The Frattini test of BS EN 196-5 (ref. 21) was conducted to determine the pozzolanic activity by chemical method. For this, 16 g of OPC 53 and 4 g of YTT were mixed with 100 ml of distilled water in a plastic bottle and sealed for 8 days at 40°C. The solution was separated by filtering the mixed sample with 2.7 μm vacuum filter paper (Whatman no. 542) above a Buchner funnel. For [OH<sup>-</sup>] and [CaO] analysis, 50 ml of filtrate solution was titrated against dilute HCl using a methyl orange indicator

**Table 3.** Compressive strength of YTT at 7 and 28 days

Test material	OPC 53 (g)	Standard sand (g)	Water (ml)	Compressive strength (MPa)	
				7 days	28 days
Control	500	1375	242	32.6	51.8
YTT	400	1375	262	25.1	40.9



**Figure 6.** Strength activity index of YTT after 7 and 28 days of curing at 23°C.

(end-point is indicated by a change in colour from yellow to orange), followed by titration with a 0.03 mol/l EDTA solution using the Patton and Reeder indicator (end-point indicated by change from purple to blue colour). The test results are presented on an isotherm curve of  $[Ca^{2+}]$ , expressed as equivalent CaO (mmol/l) versus  $[OH^-]$  (mmol/l). Test results lying below this solubility curve indicate that the sample is a pozzolan.

Donatello *et al.*<sup>22</sup> prepared lime saturation test samples by adding 1 g of pozzolan to a plastic bottle containing 75 ml of saturated lime solution. The lime solution was prepared by dissolving 2 g of hydrated lime in 1 litre of distilled water. The bottles were then sealed and placed in an oven at 40°C for 1, 3 and 7 days. At the specified ages, the CaO content was determined using the methodology described earlier. Results are reported as percentage of total CaO fixed per gram of test pozzolan with respect to time.

Table 3 provides the compressive strengths of YTT modified and control mortars at 7 and 28 days.

It is clear from the results (Table 3) that the mortar with YTT developed lower strength at 7 and 28 days compared to the OPC mortar. The reduction was possibly due to the difference in water content used for control specimen (242 ml) according to standard guidelines<sup>20</sup>. Whereas for YTT blended specimens water was found

using trial and error method based on the same flow value of control mortar (260 ml). However, ASTM C618 (ref. 23) recommends only 75% strength for pozzolanic blended mortar compared to control specimens. SAI of YTT was 76.9% at 7 days, which is above the minimum requirement in the standard to define YTT as a supplementary cementitious material (Figure 6). Furthermore, a marginal increase in the SAI (79%) was observed at 28 days compared to 7 days, which represents additional pozzolanic performance of YTT.

In the present method, 75% of the strength is only recommended as a minimum requirement to select pozzolanic materials, whereas 80% of the cement is already available in the prepared mortar specimens compared to control specimens. Therefore, the strength of the blended mortar is not only due to the pozzolanic reaction but is primarily from cement hydration. To confirm the pozzolanic performance of YTT, its direct activation with calcium hydroxide is explained below to support the observation in the strength activity test.

As stated earlier, the Frattini test and lime saturation test were also performed to determine the pozzolanic reaction in term of consumption of calcium hydroxide with respect to time. The sample used in the study for Frattini test is similar in proportion to the strength activity test (80% of OPC and 20% of YTT). The concentration of  $[OH^-]$  observed from titration of prepared filtrate against dilute HCl and that of  $[CaO]$  against EDTA titration were 50.8 and 5.03 mmol/l respectively.

The above observation was found to fall below the standard solubility curve due to reduction of calcium hydroxide that forms a strong calcium silicate hydrate bond<sup>6</sup> and this reflects a good pozzolanic performance of YTT (Figure 7). Additionally, reduction in the CaO and  $OH^-$  concentrations is a clear evidence for the consumption of calcium hydroxide in the Frattini test. According to the method<sup>21</sup>, if the material passes as a pozzolan in the test at 8 days, there is no need to evaluate it at 15 days (which is generally recommended for slowly reacting pozzolan).

To understand the percentage reduction of CaO in the given sample, Donatello *et al.*<sup>22</sup> proposed a formula with correlating concentration  $[CaO]$  and theoretical maximum  $[CaO]$  as follows.

$$[CaO] \text{ reduction } \% = \frac{\text{Maximum } [CaO] - [CaO]}{\text{Maximum } [CaO]} \times 100. \tag{1}$$

In the given sample, the theoretical maximum [CaO] was found to be 9.77 mmol/l and CaO reduction was 49.6% at 8 days. In addition, compared to the Frattini test, reduction of calcium can be easily quantified in the lime saturation test method due to direct activation of pozzolanic material with saturated lime solution without cement in the system<sup>22</sup>. The results of lime saturation test are shown in Figure 8, plotted for three different durations (1, 3 and 7 days) on the X-axis and percentage of reduction in terms of CaO concentration on the Y-axis. Figure 8 indicates that good pozzolanic reaction takes place even at day 1 with reduction of CaO up to 36.6%. Moreover, by day 3 the pozzolanic reaction is found to significantly reduce CaO (83.9%), and 96.8% of CaO is removed by 7 days. This result is clearly indicative of good pozzolanicity.

Similar observation has been reported for paper waste sludge<sup>24</sup>. In our study, comparing the observations in the Frattini test after 8 days, the rate of CaO consumption in the lime saturation test was doubled within 7 days of curing period even at the same temperature. This is because of the rich saturated lime environment in the test that enabled the maximum possible pozzolanic performance of YTT. There is no cement hydration process in lime saturation test and consumption of CaO directly represents the pozzolanic performance of YTT; similar trends for other pozzolans have been reported in the literature<sup>8,22,25</sup>.

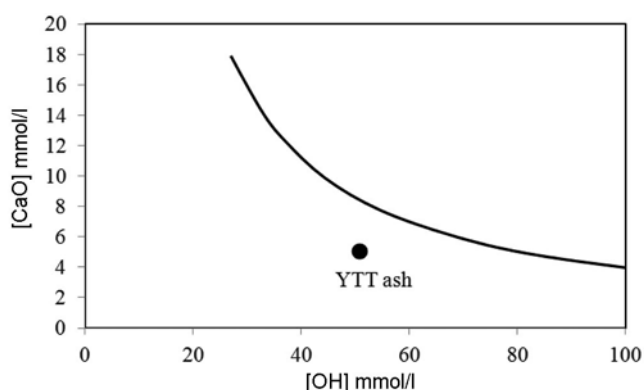


Figure 7. Frattini test results of YTT after 8 days curing at 40°C.

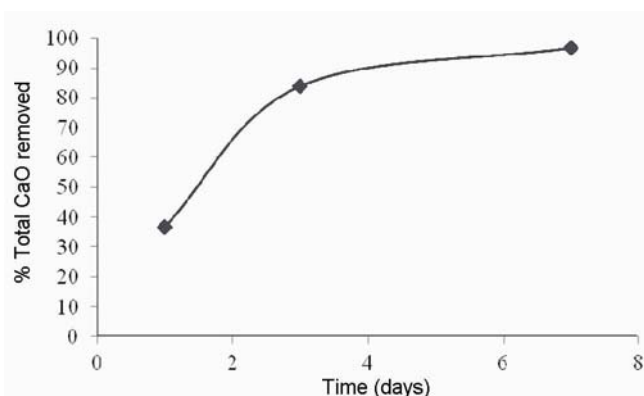


Figure 8. Lime saturation test results for YTT after 1, 3 and 7 days.

From the observations in the Frattini test and lime saturation test, the pozzolanicity of the reactive silica present in YTT can be confirmed<sup>6</sup>. On the other hand, the reduction observed in the SAI is due to different water content as stated earlier. Nevertheless, higher strength was reported for calcined clay blended specimens compared to control specimens in the strength activity test<sup>26</sup>. This is due to higher fineness of calcined clay used in that study<sup>7</sup>. However YTT used in the present study has low specific surface area (164 m<sup>2</sup>/kg) compared to cement, and further grinding may lead to significant improvement in the pozzolanic performance of YTT.

YTT occurs as a shallow subsurface deposit and can be economically mined compared to clay. In addition, YTT is a natural pozzolan and can be used directly without calcination process. On the other hand, clay needs to be calcined at higher temperature for use as a pozzolan<sup>27</sup>. Andhra Pradesh is one of the leading states in India in the production of cement and YTT in Jwalapuram is spread over an area of ~9 km<sup>2</sup> with thickness ranging from 15 cm to 2.46 m (ref. 1). Due to superior pozzolanic performance, it can be utilized as blending material in cement manufacture for the production of PPC to achieve sustainable and quality concrete.

In the present study, we have evaluated the pozzolanic nature of YTT using standard methods. The following observations have been made from the study:

(1) The particle size distribution, geochemical data and morphology studies strongly suggest that volcanic ash of the study area is positively associated with YTT eruption.

(2) Chemical characteristics of YTT satisfy the limits of fly ash in IS: 3812–1981.

(3) The compressive strength of 20% YTT blended mortars was lower than the control mortar, but the material showed higher than minimum (75%) SAI at 7 and 28 days.

(4) In the chemical assessment of pozzolanicity by the Frattini test and lime saturation test, the pozzolanic activity of YTT was clearly evident. While YTT was below the solubility limiting curve in the Frattini test, it showed a large degree of CaO fixation in the lime saturation test.

(5) Overall, the results clearly indicate that good quality PPC can be manufactured using YTT with up to 20% replacement of the cement.

1. Petraglia, M. *et al.*, Middle Paleolithic assemblages from the Indian subcontinent before and after the Toba super-eruption. *Science*, 2007, **317**, 114–116.
2. Fisher, R. V. and Schmincke, H. V., *Pyroclastic Rocks*, Springer, Berlin, 1984, p. 472.
3. Williams, M., The ~73 ka Toba super-eruption and its impact: history of a debate. *Quaternary Int.*, 2012, **258**, 19–29.
4. Dutta, M. and Mukherjee, S., An outlook into energy consumption in large scale industries in India: the cases of steel, aluminium and cement. *Energy Policy*, 2010, **38**, 7286–7298.

5. Malhotra, V. M. and Kumar Mehta, P., *Pozzolanics and Cementitious Materials*, Gordon and Breach Science Publishers, Amsterdam, 1996.
6. Antiohos, S. and Tsimas, S., Investigating the role of reactive silica in the hydration mechanisms of high-calcium fly ash/cement systems. *Cem. Concr. Compos.*, 2005, **27**, 171–181.
7. Rahhal, V. and Talero, R., Calorimetry of Portland cement with silica fume, diatomite and quartz additions. *Constr. Build. Mater.*, 2009, **23**, 3367–3374.
8. Tironi, A., Trezza, M. A., Scian, A. N. and Irassar, E. F., Assessment of pozzolanic activity of different calcined clays. *Cem. Concr. Compos.*, 2013, **37**, 319–327.
9. Bendapudi, S. C. K. and Saha, P., Contribution of fly ash to the properties of mortar and concrete. *Int. J. Earth Sci. Eng.*, 2011, **4**, 1017–1023.
10. Habert, G., Choupay, N., Escadeillas, G., Guillaume, D. and Montel, J. M., Clay content of argillite: influence on cement based mortars. *Appl. Clay Sci.*, 2009, **43**, 322–330.
11. Schulz, H., Emeis, K. C., Erlenkeuser, H., Von Rad, U. and Rolf, C., The Toba volcanic event and interstadial/stadial climates at the marine isotopic stage 5 to 4 transition in the Northern Indian Ocean. *Quaternary Res.*, 2002, **57**, 22–31.
12. Acharya, S. K. and Basu, P. C., Toba ash in the Indian subcontinent and its implications for correlation of late Pleistocene alluvium. *Quaternary Res.*, 1993, **40**, 10–19.
13. Chesner, C. A., Petrogenesis of the Toba Tuffs, Sumatra, Indonesia. *J. Petrol.*, 1998, **39**, 397–438.
14. Jones, M. T., Sparks, R. S. J. and Valdes, P. J., The climatic impact of super volcanic ash blankets. *Climate Dyn.*, 2007, **29**, 553–564.
15. Haslam, M. *et al.*, A southern Indian Middle Palaeolithic occupation surface sealed by the 74 ka Toba eruption: further evidence from Jwalapuram Locality 22. *Quaternary Int.*, 2012, **258**, 148–164.
16. Raj, R., Occurrence of volcanic ash in the Quaternary alluvial deposits, lower Narmada basin, western India. *J. Earth Syst. Sci.*, 2008, **117**, 41–48.
17. Down, M. J., Master, R. W., Streckeisen, A. and Zanetti, B., A chemical classification of volcanic rocks based on the total alkali-silica diagram. *J. Petrol.*, 1986, **27**(3), 745–750.
18. IS: 1727, Indian standard specification for methods of test for pozzolanic materials. Bureau of Indian Standards, New Delhi, 1967.
19. IS 3812, Indian standard specification for fly ash for use as pozzolana and admixtures. Bureau of Indian Standards, New Delhi, 1981.
20. ASTM C311, Standard specification for sampling and testing fly ash or natural pozzolans for use in Portland-Cement Concrete, ASTM, USA, 2002.
21. BS EN 196(5), Standard specification for testing cement – Pozzolanicity tests for pozzolanic cement, BSI, London, 2005.
22. Donatello, S., Tyrer, M. and Cheeseman, C. R., Comparison of test methods to assess pozzolanic activity. *Cem. Concr. Compos.*, 2010, **32**, 121–127.
23. ASTM C618, Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM, USA, 2003.
24. Frias, M., Villar-cocin, E. and Valencia-Morales, E., Characterisation of sugar cane straw waste as pozzolanic material for construction, calcining temperature and kinetic parameters. *Waste Manage.*, 2007, **27**, 533–538.
25. Hamidi, M., Kacimi, L., Cyr, M. and Clastres, P., Evaluation and improvement of pozzolanic activity of andesite for its use in eco-efficient cement. *Constr. Build. Mater.*, 2013, **47**, 1268–1277.
26. Tironi, A., Trezza, M. A., Scian, A. N. and Irassar, E. F., Kaolinitic calcined clays: factors affecting its performance as pozzolans. *Constr. Build. Mater.*, 2012, **28**, 276–281.
27. Janotka, I., Puertas, F., Palacios, M., Kuliffayová, M. and Varga, C., Metakaolin sand-blended-cement pastes: rheology, hydration process and mechanical properties. *Constr. Build. Mater.*, 2010, **24**, 791–824.

ACKNOWLEDGEMENTS. We thank Dr Bahurudeen (Department of Civil Engineering, IIT Madras) for technical assistance and University Grants Commission, New Delhi for providing financial assistance.

Received 18 March 2015; revised accepted 26 July 2015

doi: 10.18520/v109/i10/1869-1874