An Investigation on Pozzolanicity of Mechanically Activated Pond Ash

V Vidyadhara1*, T Shamanth Gowda1 and R V Ranganath2

1 Research Scholar, Department of Civil Engineering, BMS College of Engineering, Bengaluru, India
2 Professor, Department of Civil Engineering, BMS College of Engineering, Bengaluru, India
*vidyadhara92@outlook.com

Abstract. Pond ash (PA) is one of the major industrial solid wastes from thermal power plants. In the present study, PA of different storage durations, i.e. freshly ponded, two year ponded and Six-year ponded ash were collected from Bellary Thermal Plant (BTP). All three kinds of PA were mechanically activated by grinding in Industrial Hammer Mill. Unprocessed Pond Ash (UPA) and Ground Pond Ash (GPA) were characterised for Particle Size Distribution (PSD) by Laser-diffraction analyser. Mineralogical and Morphological characteristics were analysed through X-ray Diffraction and Electron Microscopic studies. Chemical composition of PA was analysed. The pozzolanicity of PA and other Supplementary Cementitious Materials (SCM) was determined and compared by conducting Lime reactivity test. XRD patterns and Chemical analysis clearly indicate the presence of relatively more amorphous phases in a fresh batch of PA compared to the one which is ponded for a longer duration. Lime reactivity strength (LRS) of UPA was far behind the LRS of commonly used SCM’s. Mechanical activation of PA improved the LRS from 0.57 MPa to 2.41 MPa. The results suggest the possibility of enhancing the reactivity of PA with early use and more efficient grinding process, thus add value to PA for its use in concrete.

1. Introduction
Concrete is the man-made material which is most widely used by mankind next to water in terms of substance consumption. Cement is the largely used binding material in concrete. One ton of CO₂ is released to the environment in the production of a unit ton of cement [1]. Utilisation of supplementary binding materials in concrete, especially waste materials from different industries is the current trend in concrete technology. Fly Ash, Bottom Ash, Silica Fume, Blast Furnace Slag, Paper Sludge and calcium carbide are some of the industrial waste materials used in concrete by earlier researchers [1-6]. Usage of these materials in concrete results in the reduction of its carbon footprint.

Coal Fuel ash from Thermal Power Plants has been used in concrete as admixtures to replace cement as well as aggregates. Coal ashes are of different types which include Fly ash, Bottom Ash, Ponded fly ash and Pond Ash. Fly ash is the most reactive material among all ashes, because of the presence of fine, spherical particles with a more amorphous phase. Fly ash, because of its high pozzolanic property, is used as a replacement for cement in conventional concrete [7]. In addition, due to the presence of amorphous silica and alumina, it is used as a binder material in geopolymer concrete [2]. Bottom ash is the coarser ash that is collected from the bottom of the boiler. After milling it is transported for open-disposal by simple water- wash [8]. It is less reactive compared to fly ash, as it contains coarser, porous, irregular shaped particles with fewer amorphous phases. Bottom ash is used as fine aggregate in concrete, as it comprises of well-graded, angular, rough-textured and light particles [9]. Presence of porous particles in Bottom ash makes it a better alternative to be used as coarse aggregate in pervious...
concrete [10]. Grinding of bottom ash results in the decrease of porosity and increase in the surface area thereby increasing its reactivity [11]. Ground bottom ash is used in cement mortar as partial replacement to cement [12]. The additional gain in the reactive components of bottom ash after grinding has made researchers to use it as aluminosilicate precursor in geopolymer [13]. Countries like USA and UK, dispose unused fly ash into ponds, which is termed as Ponded fly ash. Ponding fly ash in such a manner will result in increased size of particles and reduction of amorphous phase compared to virgin fly ash [14]. Ponded fly ash is used as a replacement to cement in concrete and the strengths achieved are relatively less compared to concrete made using virgin fly ash [15].

Fly ash from electrostatic precipitator which will be unused and bottom ash from boiler after milling is conveyed to ponds in the form of water mixed slurry. This stored slurry in ponds results in the generation of Pond ash [16] which is most commonly seen in Indian Thermal Power Plants. Pond ash reactivity lies in between fly ash and bottom ash as it includes reactive fine fly ash particles and non-reactive or less reactive large bottom ash particles [17]. Similar to Bottom ash, Pond ash is also used as fine aggregate in concrete since it comprises of coarser bottom ash particles. Pond ash, when used as fine aggregate, has resulted in a decrease in the workability of concrete [18]. Reduction in strength is also noticed when Pond ash is used as a partial replacement to cement in concrete [16]. However, there is a lack of research on the pozzolanic behaviour of fine ground or mechanically activated Pond ash, unlike Bottom ash. Pond ash is more reactive than bottom ash, as it contains some traces of reactive fly ash particles. There is a need for an investigation on the pozzolanicity of ground or mechanically activated pond ash so that processed Pond ash could be assessed for its potentiality to be used as a binder in conventional concrete and as aluminosilicate precursor in geopolymer concrete. The current research is an attempt to investigate the possible improvement in the pozzolanic nature of pond ash by means of simple mechanical activation technique.

2. Experimental program

2.1. Materials

Pond ash (PA) was procured from Bellary thermal power plant, Karnataka. PA of three kinds, Fresh ponded, two-year-old and Six-year-old was taken from the plant-based on their age of ponding. In addition, one more type of sample i.e. mixed sample was prepared by blending above three samples in equal proportions. All the samples of PA were oven-dried at 110±5 °C. A portion of PA from all respective samples was subjected to grinding in Industrial Hammermill. Further, Fly Ash (FA), Ultrafine Fly Ash (UFA), Ground Granulated Blast Furnace Slag (GGBS) and Ultrafine Slag (US) were purchased from commercial sources for their comparative analysis with PA. Lime was locally procured for use in Lime reactivity test. Standard sand (Ennor) [19] was used as fine Aggregate.

The Fresh Unprocessed Pond ash (FUPA), Two-year-old Unprocessed Pond ash (2UPA), Six-year-old Unprocessed Pond ash (6UPA), Blend Unprocessed Pond ash (BUPA), Fresh Ground Pond ash (FGPA), Two-year-old Ground Pond ash (2GPA), Six-year-old Ground Pond ash (6GPA) and Blend Ground Pond ash (BGPA) were checked for their pozzolanicity.

2.2. Physical properties of pond ash

The Particle Size Distribution (PSD) of all the PA samples were analysed using Laser Diffraction Analyser and PSD curves are shown in figure 1. Specific gravity, Surface area, weight retained on sieve no. 325 and mean diameter of PA particles are represented in table 1. The specific gravity of GPA is recorded more compared to UPA, as grinding eliminates the pores of PA thereby increasing mass to volume ratio. Since UPA was coarser, Surface area by Blaine’s test couldn’t be found out [3]. Blaine Surface area of GPA varies in the range of 222-288 m²/kg. Weight retained on No.325 sieve and median particle size of GPA is greatly reduced compared to UPA. Out of all unprocessed samples, 6UPA comprised of higher coarser particles. There is an overall increment in fineness of PA after subjecting it to the selected grinding process. This can be noticed from the PSD graph and from the median particle size of samples.
Table 1. Physical properties of different PA.

| Samples | Specific Gravity | Surface area (m²/kg) | % by weight Retained on a No. 325 sieve | Median Particle Size, d50 (mm) |
|---------|------------------|----------------------|----------------------------------------|------------------------------|
| FUPA    | 1.96             | -                    | 90                                     | 160                          |
| 2UPA    | 1.79             | -                    | 87                                     | 127                          |
| 6UPA    | 2.09             | -                    | 92                                     | 188                          |
| BUPA    | 1.86             | -                    | 93                                     | 156                          |
| FGPA    | 2.32             | 230                  | 62                                     | 59                           |
| 2GPA    | 2.19             | 222                  | 62                                     | 59                           |
| 6GPA    | 2.26             | 288                  | 47                                     | 40                           |
| BGPA    | 2.25             | 240                  | 55                                     | 49                           |

2.3. XRD, SEM and EDAX studies of pond ash

Before grinding, PA is observed to have porous, irregular, agglomerated -larger particles and grinding process resulted in a reduction of its size and porosity [1, 3, 12] which is clearly indicated in SEM images shown in figure 2 a) and b). XRD analysis was carried out for finding the mineralogical composition of UPA. Quartz was the main mineral phase present in PA as shown in figure 3a. Scanning was concentrated between 20° and 30° to compare the amorphous phase of different UPA. Hump formation can be noticed at 26.5° in case of FUPA and 2UPA indicative of the presence of the amorphous phase. Micrograph shown in figure 3 b) was obtained by Energy-dispersive X-ray Analysis (EDAX) for the analysis of elements in PA. The presence of Si, Al, O and Fe were confirmed as the main elements in PA as per the analysis [11].

Figure 1. Particle size distribution curves of different PA.

Figure 2. SEM images of  a) Unprocessed pond ash b) Ground pond ash.
2.4. Chemical composition of pond ash

Chemical composition of Unprocessed PA samples is given in Table 2. As per ASTM C618 [20], Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use in Concrete, $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ minimum limit should be 70% and LOI maximum limit should be 6%. Chemical composition of all the PA samples are well within the aforementioned limits and are classified as ASTM Class F ash [21]. Reactive silica content represents the percentage of amorphous silica in total silica content. FUPA has a good amount of amorphous silica and 6UPA has the lowest value of the same. This depicts, increase in ponding duration reduces the reactive silica in PA.

| Samples | LOI  | $\text{SiO}_2$ | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | $\text{CaO}$ | $\text{MgO}$ | Reactive $\text{SiO}_2$ | Reactive $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ |
|---------|------|----------------|-------------------------|-------------------------|-------------|-------------|------------------------|------------------------------------|
| FUPA    | 5.30 | 58.38         | 25.34                   | 5.68                    | 2.69        | 0.98        | 20.02                  | 89.80                              |
| 2UPA    | 3.87 | 59.24         | 26.94                   | 5.68                    | 2.24        | 1.16        | 18.74                  | 91.86                              |
| 6UPA    | 4.47 | 55.90         | 28.76                   | 5.56                    | 2.86        | 1.28        | 16.02                  | 90.22                              |
| BUPA    | 5.90 | 57.12         | 26.06                   | 5.84                    | 2.57        | 1.37        | 17.86                  | 88.98                              |

2.5. Pozzolanicity of pond ash

Pozzolanic reactivity of supplementary cementitious material (SCM) can be assessed from various tests and Indian standard IS: 1727 – 1967[22] recommends for Pozzolanic reactivity of SCM by Lime reactivity test and same was adopted in the current study. SCM, Standard sand (Ennor) [20] and Lime will be mixed with water in standard proportions. Cubes of size 50mm are cast and demoulded after 2 days. Demoulded samples are kept in desiccators for curing in an oven at standard temperature and relative humidity conditions for 8 days. Later cubes are tested for compressive strength. This test can assess the potentiality of SCM to react with Calcium Hydroxide ($\text{Ca(OH)}_2$) to form Calcium Silicate Hydrate (CSH) and Calcium Aluminate Hydrate (CAH) gels.

3. Results and discussion

3.1. Water requirement

As per lime reactivity test method IS: 1727 – 1967[22], the amount of water added to the mix should produce a flow of 170±5 mm on flow table. Water required by different PA samples to achieve the prescribed flow is given in Table 3. From Table 3, it is evident that between UPA samples and GPA samples, UPA samples consumed more water compared to GPA samples to meet the flow requirement. Since UPA samples contain porous and dry bottom ash particles, more water is absorbed demanding...
extra water for lubrication as seen in earlier studies [3, 8, 23]. Pores are eliminated after grinding, thereby reducing the water requirement in case of ground samples to maintain the same flow [12].

Table 3. Lime reactivity test results of pond ash.

| Samples | Lime reactivity 8 days (MPa) | Lime reactivity 28 days (MPa) | Water added (ml) to achieve flow of 170±5mm |
|---------|-----------------------------|-----------------------------|---------------------------------------------|
| FUPA    | 0.57                        | 0.98                        | 390                                         |
| 2UPA    | 0.60                        | 0.96                        | 390                                         |
| 6UPA    | 0.40                        | 0.71                        | 400                                         |
| BUPA    | 0.46                        | 0.96                        | 400                                         |
| FGPA    | 2.41                        | 3.35                        | 310                                         |
| 2GPA    | 2.22                        | 3.01                        | 310                                         |
| 6GPA    | 2.14                        | 3.05                        | 320                                         |
| BGPA    | 2.38                        | 3.13                        | 320                                         |

3.2. Lime reactivity strength (LRS)

LRS as observed from table 3 records low values for UPA samples compared to that of GPA. The strength is evaluated after 8 and 28 days of desiccator curing and the results are graphically represented in figure 4. Even though UPA was rich in Silica and alumina, due to more coarser and porous particles with less specific surface area, it has resulted in a lesser degree of reaction of silica and alumina with Ca(OH)$_2$. In contrast, grinding resulted in eliminating pores, reducing size, increasing both surface area and reactive silica content in PA particles, as observed in studies on mechanical activation of red mud [24]. Thus the degree of reaction of silica and alumina present in GPA with Ca(OH)$_2$ was relatively more contributing for higher strength both at 8$^{th}$ and 28$^{th}$ day of testing. In addition to increased reactivity, non-reactive GPA particles contribute strength by filling the voids in the matrix.

Among UPA samples 6UPA samples got lesser LRS, because Six years of Ponding resulted in an increase in the size of their particles as well as a decrease in reactive silica content which can be observed from PSD graph (Figure 1) and chemical composition (Table 2). Among the GPA samples, 6GPA had finer particles compared to other samples, in spite of this LRS of 6GPA was less compared to FGPA which is having higher reactive silica content. It clearly indicates in addition to size reduction, the presence of silica in amorphous phase (Reactive silica) is obligatory for a higher degree of pozzolanic reaction [12].

SEM images shown in figure 5 a, further verifies the reason for Lower LRS due to presence of more unreactive coarser PA particles in case of unprocessed PA [17]. Whereas for ground PA, a relatively dense matrix with more reacted phase can be noticed from figure 5 b.

Figure 4. Graph showing lime reactivity strength results of different PA.
3.3. **Comparison of lime reactivity strength**

It can be observed from the LRS of SCMs shown in table 4, the reactivity of popular SCMs is more prominent compared to PA. However, after certain mechanical activation, the reactivity of PA is improved over that of UPA. The reduction in particle size as recorded from figure 2 may have created more reactive phases of silica and alumina after processing [24]. Yet the comparative reactivity is less than the commercial mineral admixtures. This indicates that with a better grinding process and a further reduction in Particle size of raw PA, the pozzolanic behaviour may be made equivalent to that of FA which is noticed in earlier studies on pozzolanicity of bottom ash [12].

Considering the microstructure of LR specimen, it is clear that commercial SCMs such as FA, UFA, GGBS and UFS have a denser matrix (Figure 6) compared to PA samples (Figure 5).

![Figure 5. SEM images of lime reactivity tested specimens of a) UPA b) GPA.](image)

![Figure 6. SEM images of lime reactivity tested specimens of a) FA b) UFA c) GGBS d) UFS.](image)
Table 4. Lime reactivity strength of SCMs and PA.

| Samples                        | Lime reactivity 8 days (MPa) |
|--------------------------------|------------------------------|
| Ultrafine Slag                | 13.46                        |
| Ground Granulated Blast Furnace Slag | 7.21                      |
| Ultrafine Fly Ash             | 6.70                         |
| Fly Ash                       | 5.33                         |
| UPA                           | 0.46                         |
| GPA                           | 2.38                         |

4. Conclusions
The brief characterisation of abundantly available PA along with LR test results has indicated the possibility of utilising the same in cement composites. Simple mechanical activation procedure adopted in the current study has shown promising results towards enhancing the reactivity of PA for its large-scale utilisation.

- PSD curves and SEM analysis of both UPA and GPA indicate reduced particle size after processing that can induce reactivity and better filling ability of PA particles when used in heterogeneous material like concrete.
- XRD and Chemical analysis of PA indicates the reduction in its reactivity with longer storage period in ponds and hence it is of benefit to use PA as early as possible from the period of discharge. Based on Chemical analysis result PA may be classified as ASTM Class F ash.
- Results of LRS of GPA have confirmed increased pozzolanic reactivity compared to UPA. The increment in strength is recorded to be around 5 times that of UPA as on 8\textsuperscript{th} day of incubation of test specimens. The strength gain has continued even up to 28\textsuperscript{th} day of incubation for GPA samples which are 3 to 4 times higher than that of UPA samples.
- The comparative pozzolanic reactivity of PA even after grinding is recorded lesser than that of common SCMs. However, the study suggests the possibility of enhancing the reactivity of PA by early use after disposal along with the efficient grinding process, thus adding value to PA for its use in concrete.

5. References
[1] Penpichcha Khongpermgoso, Akkadath Abdulmatin, Weerachart Tangchirapat and Chai Jaturapatitakkul 2019 Evaluation of compressive strength and resistance of chloride ingress of concrete using a novel binder from ground coal bottom ash and ground Calcium carbide residue Construction and Building Materials 214 631–40
[2] Prinya Chindaprasirt, Chai Jaturapatitakkul, Wichian Chalee and Ubolluk Rattanasak 2009 Comparative study on the characteristics of fly ash and bottom ash geopolymers Waste Management 29 539–43
[3] Chai Jaturapatitaku and Raungrut Cheerarot 2003 Development of Bottom Ash as Pozzolanic Material Journal of Materials in Civil Engineering 15(1) 48–53
[4] Hisham M Khater 2013 Effect of silica fume on the characterisation of the geopolymer materials International Journal of Advanced Structural Engineering 5 12
[5] Zhuguo li and Sha li 2018 Carbonation resistance of fly ash and blast furnace slag based geopolymor concrete Construction and Building Materials 163 668–80
[6] Rozineide A Antunes Boca Santa, Adriano Michael Bernardin, Humberto Gracher Riella and Nivaldo Cabral Kuhnen 2013 Geopolymer synthetised from bottom coal ash and calcined paper Sludge Journal of Cleaner Production 57 302–7
[7] Manomi N, Sathyan D, Anand K B 2018 Coupled effect of superplasticiser dosage and fly ash content on strength and durability of concrete Materials Today: Proceedings vol 5 pp 24033–42
[8] Ng H J, Al Bakri Abdullah M M, Tan S J, Sandu A V and Hussin K 2018 Characterisation and understanding of Portland cement mortar with different sizes of bottom ash Advances in Cement Research 30(2) 66–74

[9] Iman M Nikbin, Saman Rahimi R, Hamed Allahyari and Mohammad Damadi 2016 A comprehensive analytical study on the mechanical properties of concrete containing waste bottom ash as natural aggregate replacement Construction and Building Materials 121 746–59

[10] Yuwadee Zaetang, Ampol Wongsa, Vanchai Sata and Prinya Chindaprasirt 2015 Use of coal ash as geopolymer binder and coarse aggregate in pervious concrete Construction and Building Materials 96 289–95

[11] Rozineide A, Antunes Boca Santa, Cintia Soares and Humberto Gracher Riella 2017 Geopolymers obtained from bottom ash as source of aluminosilicate cured at room temperature Construction and Building Materials 157 459–66

[12] Akkadath Abdulmatin, Weerachart Tangchirapat and Chai Jaturapatkakkul 2018 An investigation of bottom ash as a pozzolanic material Construction and Building Materials 186 155–62

[13] Vanchai Sata, Apha Sathonsaowaphak and Prinya Chindaprasirt 2012 Resistance of lignite bottom ash geopolymer mortar to sulfate and sulfuric acid attack Cement & Concrete Composites 34 700–8

[14] Tarunjit Singh Butalia 2019 Beneficial use of ponded fly ash in structural concrete UKIERI Concrete Congress Key Note Address (Dr B R Ambedkar National Institute of Technology Jalandhar) https://ukiericoncretecongress.com/Home/files/Proceedings/pdf/1B-T%20Butalia-Keynote-Conf-1.pdf

[15] M J McCarthy, L Zheng, R K Dhir and G Tella 2018 Dry-processing of long-term wet-stored fly ash for use as an addition in concrete Cement and Concrete Composites 92 205–15

[16] A Sofi and B R Phanikumar 2015 An experimental investigation on flexural behaviour of fibre-reinforced pond ash-modified concrete Ain Shams Engineering Journal 6 1133–42

[17] R V Ranganath, B Bhattacharjee, and S Krishnamoorthy 1998 Influence of size fraction of ponded ash on its pozzolanic activity Cement and Concrete Research 28(5) 749–61

[18] Ranganath R V 1995 A study on the characterisation and use of Ponded Fly Ash as Fine Aggregate in Mortar and Concrete Ph.D Thesis Report (IITD–Delhi)

[19] Bureau of Indian Standards 2002 IS 650: Specification for Standard Sand for Testing of Cement (New Delhi India)

[20] American Society for Testing and Materials 2015 ASTM C618 Standard specification for coal fly ash and raw or calcined natural pozzolans for use in concrete (ASTM International, West Conshohocken, PA)

[21] M Cheriaf, J Cavalcante Rocha and J Péra 1999 Pozzolanic properties of pulverised coal combustion bottom ash Cement and Concrete Research 29 1387–91

[22] Bureau of Indian Standards 1996 IS :1727-1967 Methods of test for pozzolanic materials (New Delhi India)

[23] Apha Sathonsaowaphaka, Prinya Chindaprasirta and Kedsarin Pimraksab 2009 Workability and strength of lignite bottom ash geopolymer mortar Journal of Hazardous Materials 168 44–50

[24] Smita Singh, M U Aswath and R V Ranganath 2018 Effect of mechanical activation of red mud on the strength of geopolymer binder Construction and Building Materials 177 91–101