Influence of Coal Ash on the Concrete Properties and Its Performance Under Sulphate and Chloride Conditions

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Abstract

This study investigated the influence of Coal Bottom Ash (CBA) on the concrete properties and evaluate the effects of combined exposure of sulphate and chloride conditions on the concrete containing CBA. During concrete mixing, cement was replaced with CBA by 10% of cement weight. Initially, concrete samples were kept in normal water for 28 days. Next, the specimens were moved to combined solution of 5% Sodium sulphate (Na_2SO_4) and 5% sodium chloride (NaCl) solution for further 28 to 180 days. The experimental findings demonstrated that the concrete containing 10% CBA (M2) gives 12% higher compressive strength than the water cured normal concrete (M1). However, when it was exposed to solution of 5% Na_2SO_4 and 5% NaCl , gives 0.2% greater compressive strength with reference to M1. The presence of 10% CBA decreases the chloride penetration and drying shrinkage around 33.6% and 29.2% respectively at 180 days. Hence, this study declared 10% CBA as optimum that can be used for future research.

1. Introduction

Coal is a source of energy to produce electricity. The burning of coal in a furnace of a power plant, results in the generation of noncombustible ashes like coal bottom ash (CBA) and fly ash (FA). Typically one megawatt electricity is produced through 15–18.75 tons burning of coal and left behind around 4.3 tons of CBA and 11 tons of FA (Asokan, Saxena, & Asolekar, 2005). Approximately annual coal ash generation is about 600–800 million tons worldwide (Hui, Hui, & Lee, 2009). Coal ash that is removed from flue gases in an electro-precipitator is named as FA which is around 70–80% of total ash and remaining 20–30% of heavyweight ash falls in to the bottom of furnace, called as CBA (Singh, Siddique, Ait-Mokhtar, & Belarbi, 2015). In America, the coal-fired power plants produces around 22.6 million tons of FA and 3.8 million of CBA (ACAA, 2017), particularly Malaysian power plants contributes around 6.8 million tons of FA and about 1.7 million tons of CBA annually (Rafieizonooz, Mirza, Salim, Hussin, & Khankhaje, 2016) and in Indian around 155 power plants are operated on coal and produces approximately 169.25 million tons of FA and 34 million tons of CBA (CEA, 2017). It was reported by Central Electricity Authority, New Delhi that the fly ash is almost 63.28% utilized for different purposes i.e., concrete, cement, earth filling, masonry, road embankments, agriculture, and others (CEA, 2017). However, high volume of fly ash is already utilized in the concrete (Hooton, Naik, Ramme, & Tews, 1994) (Jayaranjan, van Hullebusch, & Annachhatre, 2014) and it was recognized as a cement constituent and standardized vide BS EN 197-1 (2011). It is also adopted in cement manufacture; to conquer the problem carbon dioxide (CO_2) emissions in the environment. However, the use of CBA is still unexplored, and it is being directly disposed-off in to the open ponds which occupies huge land area and contaminated the soil and underground water resources (IDEM, 2017). According to the Physicians for social responsibility (PSR) (United States Affiliate of International Physicians for the Prevention of Nuclear War, 1985) declared that coal ash has a dangerous and toxic material in storage and disposal under wet condition, but they suggested that dry storage should be for extreme command to avoid leaching, moving or leakage of toxicants. The use coal for the electricity generation has require efforts to manage the safe storage, disposal, and reuse of huge

amount of coal ash, therefore more research is required to be carried out on the possible use of CBA in concrete construction as to minimize the environmental pollution (Deonarine, Kolker, & Doughten, 2015). CBA is a porous in nature and dark gray in color and after grinding it poses fine particles as presented in Fig. 1. The chemical characteristics of CBA and fly ash are almost similar, but coarser than fly ash. The CBA particles mostly fall in the range of 4.75 mm to 90 μm (Singh et al., 2015). The particles size of CBA are coarser and almost comparable to that of fine aggregate due to that CBA is formerly considered as sand replacement material in concrete, which causes the reduction in compressive strength of concrete (Singh & Siddique, 2016). However, after grinding process, it offers good opportunity to be applied as cement, which could deliver better compressive strength (Mangi, Wan Ibrahim, Jamaluddin, Arshad, & Putra Jaya, 2018a) (Khan & Ganesh, 2016). But its performance may be affected in the aggressive environment that represents marine environment such as combined condition of sulphate and chloride.

Presently, the performance of concrete structure under aggressive conditions is a challenging task for the engineers and solutions for that problem is become more popular. Limited studies have been stated on the concrete with supplementary cementitious material (SCM) under combined effects of sulphate and chloride. Review of literature on the concrete comprising different SCM under sulphate and chloride attacks are summaries in Table 1.

Table 1
Previous studies

Ref.	Description	Na ₂ SO ₄	NaCl	Na ₂ SO ₄ + NaCl	Key findings
(Maes & De Belie, 2014)	Concrete containing blast-furnace slag (BFS)	5%	5%	-	Chloride penetration increased as sulphate content increased. Sulphate attack is mitigated by the presence of chloride.
(Mangi, Wan Ibrahim, Jamaluddin, Arshad, & Putra Jaya, 2018b)	Concrete containing 10% CBA	5%	5%	-	CBA has substantial potential to reduce sulphate and chloride effects in individual solution
(Snelson & Kinuthia, 2010)	Mortar containing pulverized fuel ash (PFA)	5%	-	-	PFA gives good sulphate resistance
(Sata, Sathonsaowaphak, & Chindaprasit, 2012)	Mortar containing fly ash and lignite bottom ash.	-	5%	-	Bottom ash mortars deliver good performance, and it is less susceptible to sodium sulphate
(Okoye, Prakash, & Singh, 2017)	Concrete with fly ash with silica fume	-	5%	-	Concrete containing silica fume in sulfuric acid and chloride solution gives satisfactory and higher performance as compared to control specimen.
(Kazi Tani et al., 2018)	Mortar incorporated polyethylene terephthalate (PET)	5%	-	-	PET blend cement reduces the effects of Na ₂ SO ₄
(Stroh, Meng, & Emmerling, 2016)	Fly ash concrete with granulated blast furnace slag	0.3%	2%	1.5%	Rapid access and Friedel's salt formation due to binding of chloride ions by alumina. Ettringite formation due to sulphate ions. Formation of gypsum and depletion in pH due to sulphate react with portlandite. Low pH leads to depletion in Friedel's salt.

Maes & De Belie, (2014) investigated the sulphate-chloride combined effect on the concrete containing blast-furnace slag as cement. They declared that chloride penetration increased as sulphate content increased but sulphate attack is mitigated by the presence of chloride. Furthermore, Mangi et al., (2018b) investigated individual effects of sodium sulphate and sodium chloride on concrete containing CBA. They were acknowledged that CBA has substantial potential to reduce sulphate and chloride effects in individual solution. Besides that, Snelson & Kinuthia, (2010) considered pulverized fuel ash (PFA) as cement replacement in the mortar. It was soaking in sodium sulphate solution for 504 days. They found that mortar with PFA gives good sulphate resistance.

Considering the performance of geopolymer mortars containing lignite bottom ash exposed to 3% sulfuric acid and 5% sodium sulphate solutions, it was investigated by Sata et al., (2012) that bottom ash mortars delivers good performance and it is less susceptible to sodium sulphate and sulfuric acid solutions. Okoye et al., (2017) evaluated geopolymer concrete containing fly ash and silica fume, exposed to 2% sulfuric acid and 5% sodium chloride solutions. Strength was declined around 36% and 8% in control mix and concrete with fly ash and silica fume when exposed to 2% H_2SO_4 at 90 days. Compressive strengths was declined around 18% and 0% in control mix and concrete containing fly ash and silica fume when exposed to 5% NaCl at 90 days. Hence, concrete including silica fume in sulfuric acid and chloride solution gives satisfactory and higher performance than the control mix.

Stroh et al., (2016) considered concrete with fly ash and slag exposed to combined attack of sulphate and chloride at laboratory conditions with NaCl and Na_2SO_4 solution different concentration. They declared that rapid access and binding of chloride ions by alumina, causing Friedel's salt formation. However, more sulphate ions encourage to ettringite formation and sulphate react partially with portlandite creating gypsum and pH depletion. Low pH leads to depletion in Friedel's salt. Moreover, Kazi Tani et al., (2018) evaluated influence polyethylene terephthalate (PET) on the concrete performance when exposed to 5% sodium sulphate (Na_2SO_4). They declared that PET blend cement reduces the effects of Na_2SO_4 . Modified concrete / mortars need to be introduced and investigated for the better environment and sustainable development.

The literature review indicated that the earlier studies were conducted on single solution exposure of sulphate or chloride and rare studies were found on combined effects of sulphate and chloride solution. However, the actual conditions are the different than the individual solutions. Most of the real structures are exposed to the collective solutions, especially under marine environment. Therefore, the novel appraisal of this study is to investigate performance of concrete incorporated ground CBA exposed to the combined solution of sulphate and chloride, which solutions represents the marine environment.

2. Experimental Methodology

2.1. Materials

Ordinary Portland Cement (OPC) accordance with BS EN 197-1, (2011) having consistency as 30%, initial setting time 90 minutes, final setting time 270 minutes and specific gravity 3.10 was used. The CBA obtained from a thermal power station, Selangor, Malaysia was used as OPC replacement. Original CBA was grinding for 20 hours in a ball mill grinder as shown in Fig. 2. The chemical characteristics of OPC and CBA was assessed through X-Ray fluorescence (XRF) test refer Table 2. However, it was found that the CBA is rich in SiO_2 , Al_2O_3 , Fe_2O_3 and its collective sum is around 78.4% which is greater than 70%. Hence, CBA is characterized as Class F ash with reference to ASTM C618 standard (ASTM C618-05, 2005). In addition to that, the particle size of OPC and CBA was also evaluated through Particle Size Analyzer (PSA) and results are provided in Fig. 3. It was observed through the PSA that OPC is finer than ground CBA. The OPC particles were fall in the range of 3.8 μm to 21.2 μm , whereas CBA particles were in the range of 3.7 μm to 50.5 μm . However, the specific gravity of OPC and CBA were recorded as 3.10 and 2.41, respectively. Additionally, Scanning Electron Microscope (SEM) of CBA is also provided in Figure. 4, which shows CBA particle shapes, indicated as irregular, sharp and spherical particles.

Table 2
Physical and chemical characteristics of OPC and CBA

Content (%)	O.P.C	C.B.A
SiO_2	20.6	52.5
Al_2O_3	3.9	17.6
Fe_2O_3	3.5	8.3
CaO	63.9	4.7
TiO_2	0.2	2.2
K_2O	-	0.8
MgO	1.9	0.6
SrO	-	0.2
P_2O_5	-	0.3
SO_3	3.6	0.8
Loss on ignition (LOI)	2.2	4.0
Sp. gravity	3.1	2.4
Sp. surface area (cm^2/g)	4871	3836
Size of particles (μm)	min 0.04, max 71	min 0.04, max 170

2.2. Concrete mix

The scope of this study is to involve 10% CBA as SCM, it was also formerly recommended as an optimum proportion in concrete production (Mangi et al., 2018a) (Mangi et al., 2019). Therefore, two concrete mixes were prepared with a fixed water to binder ratio (w/b) 0.5. First mix containing 100% OPC and second mix were incorporated 10% CBA as SCM. Fine aggregates passing from 5 mm sieve, coarse aggregates nominal maximum size of 10 mm was used in this study. The ACI method was used to prepare concrete mix proportions as shown in Table 3.

Table 3
Concrete mix details kg/m³

Ingredients	Control mix concrete	Concrete incorporated CBA
	M1	M2
Cement	440.0	396.0
CBA	0.00	44.0
Fine aggregates	805.0	805.0
Coarse aggregates	828.0	828.0
Water	220.0	220.0

2.3 Scope of study

This study evaluated performance of concrete incorporated CBA under sulphate-chloride conditions. Three groups of specimens were prepared as shown in Table 4. Group-I specimens; initially kept in normal water for 28 days to achieve targeted compressive strength 35MPa. Afterward, specimens were transferred into 5% Na₂SO₄ + 5% NaCl solution and compressive strength test were performed at 28, 56, 90 and 180 days. Next, Group-II specimens; were cured in normal water and RCPT testing were performed at 28 and 180 days. Group-III specimens; initially cured in normal water for 7 days as per ASTM C596 (ASTM C596, 2010), afterward specimens were kept at the room ambient temperature and drying shrinkage readings were takes at 1, 3, 7, 14, 28, 56, 90 and 180 days. Figure 5 shows the experimental set-up for compressive strength, RCPT instrument and drying shrinkage instrument.

Table 4
Specimens prepared for the study.

Group	Shape and Dimensions	Purpose	Quantity
I	Concrete Cubes Length 100 mm, width 100 and depth 100 mm	Compressive strength test	30
II	Concrete cylinders Diameter 100 mm, length 200 mm	Rapid chloride permeability test	6
III	Concrete prisms Cross-Sect. 100 mm, length 300 mm	Drying shrinkage	6

3 Results And Discussion

3.1 Compressive strength performance

To evaluate the pozzolanic reaction of CBA in concrete, the specimens were prepared with 10% CBA as a replacement of OPC. Moreover, specimens were cured in normal water and combined solution of 5% sodium sulphate (Na_2SO_4) and 5% sodium chloride (NaCl). Experimental results are summaries in Table 5 and Fig. 6, demonstrated the compressive strength relationship with respect to exposure period concrete, while Fig. 7, indicated the percentage variation in compressive strength under normal water and combined solution of 5% Na_2SO_4 + 5% NaCl .

It was observed that performance of M2 under normal water was found to be superior to M1. At the early days, the compressive strength of M2 was lower than M1, because pozzolanic reaction yet not initiated, then at 56 day and onwards, compressive strength of M2 was noticed greater than M1. It was noticed that the hydration process is affected due to CBA in concrete due to reduction in the amount of $\text{Ca}(\text{OH})_2$ (Jaturapitakkul & Cheerarot, 2003). However, M2 concrete which contained 10% ground CBA cured in normal water gives the compressive strength 60.0 MPa at 180 days, which is almost 12% greater than the control mix (M1) concrete. While same concrete gives 0.2% higher compressive strength when exposed to combined solution of 5% Na_2SO_4 + 5% NaCl at 180 days. It was observed that M1 concrete when exposed to combined 5% Na_2SO_4 + 5% NaCl solution, reduces its strength from 44 MPa to 40.6 MPa at the age of 28 days and 55.3 MPa to 51.05 MPa at the 90 days, this is due to reduction in binding ability in presence of sulphate-chloride condition. Previously, it was explained that the binding of incoming sulphate ions consequences in the formation of ettringite and gypsum (De Weerd & Justnes, 2015). Formation of Ettringite in first phase until bonding capacity of alumina is depleted according to below principal (Stroh et al., 2016) Eq. (1):

It was also observed in this study that control mix (M1) concrete, when exposed to combined solution of 5%Na₂SO₄ + 5%NaCl, losses its binding ability. Whereas M2 concrete which containing 10% CBA, enhances the silica and alumina content in the cement paste and resulting in the development of compressive strength.

Table 5
Compressive strength and percentage variation in compressive strength

Exposure period (days)	Exposed to normal water		Exposed to 5%Na ₂ SO ₄ + 5%NaCl	
	M1 (MPa)	M2 (MPa)	M1 (MPa)	M2 (MPa)
28	46.8	43.5	44.0	40.6
56	50.8	53.2	51.9	51.7
90	52.1	58.00	55.3	51.05
180	53.6	60.00	52.7	52.8

3.2 Micrograph and X-ray diffraction (XRD) Analysis

Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) technique were adopted to analyse the problems associated to the concrete when it was exposed to the combined sulphate-chloride at 180 days. Figure 8 shows the condition of control mix (M1) concrete exposed to combined solution of 5%Na₂SO₄ and 5%NaCl. Whereas Fig. 9 shows the condition of concrete with 10% CBA (M2) exposed to combined solution of 5%Na₂SO₄ and 5%NaCl. Micrograph of M1 and M2 concrete indicated two major features. One is the holding salts and second is the formation of C-S-H gel. The reduction in concrete strength is mainly caused by less formation of C-S-H gel (Aggarwal & Siddique, 2014). The formation of C-S-H gel is retarded due to salt of sulphate and chloride. It was observed that concrete with CBA (M2) has well formation of C-S-H gel as compared to normal concrete (M1).

Furthermore, it was observed that the amount of calcium silicate was found higher in control mix (CM) as compared to concrete containing CBA. The presence of CBA in concrete produces more C-S-H gel. Since CBA is high in aluminium and OPC paste is high in calcium carbonate, which makes reaction among these two compounds and form tricalcium aluminate (C₃A) and gives the adequate strength development. However, the development of ettringites (hydrous calcium aluminium sulphate) formation gives the good strength as the volume of voids were occupied by the ettringites (Aggarwal & Siddique, 2014). Moreover, the CM exposed to combined solution of 5%Na₂SO₄ + 5%NaCl was found to be more sever. Because the presence of NaCl salts produces chloro-aluminate in chloride solutions and

deterioration takes place by de-calcifications, that was noticed in all specimens. It was noticed that the hydration of cement formed different products such as quartz (SiO_2), portlandite (calcium hydroxide), belite (C_2S), alite (C_3S), calcium silicate hydrate (CSH), C_3A (tricalcium aluminate) and ettringite ($\text{C}_3\text{A}(\text{CS})\text{H}_{32}$). The pozzolanic reaction was detected in the concrete containing CBA, reaction among $\text{Ca}(\text{OH})_2$ (calcium-hydroxide). It shows that CBA could create well shape CSH gel which delivered higher compressive strength performances.

3.3 Chloride penetration performance

The durability of concrete can be assessed through Rapid Chloride Penetration Test (RCPT). It is necessary to check chloride penetrability when concrete structure is built within the chloride environment. In this study, involves CBA as Supplementary Cementitious Material in concrete. However, CBA contains 17.65% aluminium oxide (Al_2O_3) and OPC contains 3.95%, which means that concrete containing CBA (M2) holds more amount of Al_2O_3 . Therefore, chlorides physically and chemically bound due to adsorption on the surface of hydrates C-S-H and C-A-H. Addition of CBA, increases the amount of Al_2O_3 , which gives the better chloride binding ability (Argiz, Moragues, & Menéndez, 2018). Besides that, fine particle of CBA also fills the free pore (Argiz, Sanjuán, & Menéndez, 2017). These phenomenal change gives the lower penetration of chloride ions through the concrete incorporated 10% CBA. It was observed that concrete with 10% CBA (M2) gives the lower chloride penetration as the age of concrete increased. It was observed from the Fig. 10, that the control mix (M1) concrete gives higher values than the high category as per ASTM C1202 (ASTM.C1202, 2006) whereas, M2 concrete gives around 33.6% lower chloride penetration than the M1 at the age of 180 days.

3.4 Drying shrinkage performance

This study evaluated the effect of CBA on the drying shrinkage (DS) of concrete was also evaluated. However, it was previously noticed that the shrinkage occurred in first two months and for later age, very less variation in shrinkage of concrete (Saha, 2018). It was experimentally known that the DS in the control mix (M1) is higher than the concrete containing 10% CBA (M2) even up to 180 days as shown in Fig. 11. The DS is significantly depending on the fineness of supplementary cementing materials (SCM), it was formerly noticed that concrete containing fly ash nano-particle, gives the higher DS (Gao, He, Li, Tang, & Qu, 2017) and DS decreases when the coarser fly ash was used (Saha, 2018). The DS in concrete containing 10%CBA (M2) were noticed lower than control mix (M1), which validated that ground CBA particle are coarser than the Ordinary Portland Cement (OPC). However, CBA addition as SCM, reduces the CaO contained in the cement paste which leading towards reduction in hydration process. Thus, lower DS was recorded in M2 as compared to M1.

Conclusions

This study declared CBA as supplementary cementitious material (SCM) due to presence of substantial proportion of three main oxides i.e. silica, alumina and ferrous. Following conclusions can be drawn.

- i. Concrete incorporated 10% CBA gives 12% higher compressive strength than normal concrete cured in normal water. Once it was exposed to combined solution of sulphate-chloride it gives around 0.2% higher compressive strength as compared to normal concrete.
- ii. It was detected through micrographs that concrete containing CBA has well formation of C-S-H gel as compared to the control mix concrete. However, the development in the strength was noticed.
- iii. Incorporation of 10% CBA in concrete reduces the chloride penetration around 33.6% at the age of 180 days. It indicated that CBA could be utilized in concrete to enhance the durability performance of concrete.
- iv. Concrete containing 10% CBA exhibits around 29.2% lower drying shrinkage as compared to the normal concrete at the age of 180 days.

It was observed that the replacement of cement with CBA offers the technical and environmental advantages, which are considered as important aspects in the sustainable concrete construction. However, this study considered samples under submerged conditions and future studies could be considered wetting and drying conditions.

Declarations

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Authors Contributions

Sajjad Ali Mangi: Preparation of original draft, experimental performance, analysis.

Mohd Haziman Wan Ibrahim: Supervision, methodology.

Norwati Jamaluddin: Review and Proof reading

Mohd Fadzil Arshad: Review

Shabir Hussain Khahro: Review and Editing

Ramadhansyah Putra Jaya: Review

Availability of data and Material

Locally available materials were used in this study.

Compliance with ethical standards

All ethical standards have been followed during this research.

Consent to participate.

Not Applicable

Consent to Publish.

Not Applicable

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Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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Figures

Figure 1

a) Original CBA, b) Ground CBA

Figure 2

Grinding process for the preparation of CBA

Figure 3

Particle size of OPC and CBA

Figure 4

SEM image of coal bottom ash

Figure 5

Experimental set-up, a) Compressive test, b) RCPT instrument, c) Drying shrinkage instrument

Figure 6

Compressive strength performance of concrete with and without CBA

Figure 7

Compressive strength percentage variation of M2 as compared to M1

Figure 8

SEM image of the concrete without CBA exposed to combined solution of $\text{Na}_2\text{SO}_4 + \text{NaCl}$

Figure 9

SEM image of the concrete with CBA exposed to combined solution of Na2SO4 + NaCl

Figure 10

XRD diffraction pattern of CM concrete exposed to 5%Na2SO4+5%NaCl

Figure 11

XRD diffraction pattern of concrete with CBA exposed to 5%Na2SO4+5%NaCl

Figure 12

Chloride penetration performance of concrete with and without CBA

Figure 13

Drying shrinkage performance of concrete with and without CBA