

Conversion of Landfilled Ash into Hydraulic Cements under Different Environments

Xuefang Wang¹, Kaize Zhu², Salina Ramli², Liwei Xu³, Faris Matakah², Parviz Soroushian^{2,4} and Anagi M Balachandra^{4*}

¹College of Civil Engineering, Fuzhou University, Fuzhou, Fujian, PR China

²Department of Civil and Environmental Engineering, Michigan State University, 3546 Engineering Building, E. Lansing, MI, USA

³College of Civil Engineering, Fujian University of Technology, 3 Xueyuan Road, University Town, Fuzhou, Fujian, China

⁴Metna Co., 1926 Turner St., Lansing, MI, USA

*Corresponding author: Balachandra AM, Metna Co., 1926 Turner Street, Lansing, MI, USA, Tel: 1+ (517) 485-1402; E-mail: abmetnaco@gmail.com

Received: October 05, 2017; Accepted: October 26, 2017; Published: November 06, 2017

Copyright: © 2017 Wang X, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Abstract

A landfilled coal fly ash was blended with different constituents for achieving a balanced chemistry that suits production of hydraulic cement and concurrent capture of carbon dioxide. The blend of raw materials was processed via input of mechanical energy into hydraulic cements. The input of mechanical energy via milling was performed in three different environments: air, N₂ and CO₂. The resultant hydraulic cements were characterized through assessment of their specific surface area, microstructure (scanning electron microscopy), chemical bond environment (FTIR), heat of hydration, and pH, total dissolved solids and electric conductivity of their solutions. Mechanical processing of the blend of raw materials was found to transform them into hydraulic cement. The environment of mechanical processing was also found to be an important factor influencing the properties of the resultant cement.

Keywords: Landfilled coal fly ash; Mechanical processing; Hydraulic cement; Alkali activation; Mineral carbonation; Capture of carbon dioxide

Introduction

Landfilled coal ash is predominantly fly ash with some bottom ash content. Coal ash is disposed of in landfills either directly or after a period of wet impoundment [1]. Significant quantities of coal ash have been accumulated in landfills over several decades. In the United States, close to 40 million tons of coal ash are disposed of in landfills annually [2]. The landfilled quantities of coal ash in Europe are of the same order of magnitude as in the United States [3].

Coal fly ash has found applications as pozzolan (partial replacement for cement) in Portland cement concrete. Coal fly ash can also be activated with alkalis for production of geopolymer concrete, that is more sustainable than Portland cement concrete [4], and also offers improved durability [5]. The need for curing of the existing classes of geopolymer concrete at elevated temperatures, however, limits their market acceptance [6,7]. Mechanical activation of coal fly ash in the presence of alkalis can reduce the need for thermal curing of alkali activated coal ash. It has been observed that grinding of landfilled coal fly ash improves the uniaxial compressive strength of alkali-activated fly ash from 2.01 MPa (raw fly ash) to 22 MPa (activated fly ash) [8]. Another investigation demonstrated that, after mechanical activation of coal fly ash, NaOH-activated ash could produce a viable compressive strength of 23 MPa after 28 days of room-temperature curing [9]. Similar results were produced in another investigation where 80% gain in the compressive strength of alkali-activated fly ash subjected to room-temperature curing was realized once the ash was subjected to mechanical activation [10]. Previously a method was developed for capture of carbon dioxide (directly from combustion emissions) into

land filled coal ash, and simultaneous transformation of the carbon dioxide and ash with supplementary minerals into a hydraulic binder for heavy metal stabilization [11]. There is further evidence reported in the literature, suggesting that mechanical activation of fly ash via grinding significantly improves the mechanical properties of alkali-activated ash [12]. It has been reported that the compressive strength of Cu-Ni slag geopolymer with the slag milled in CO₂ is higher than that obtained with slag milled in air, which was attributed to higher reactivity of the slag particles induced by chemisorption of carbon dioxide molecules in the form of distorted carbonate ions in the course of mechanical activation [13,14]. Other investigations have confirmed that the reactivity of slag can be enhanced by grinding in a carbon dioxide atmosphere, producing higher compressive strengths upon alkali activation [15,16].

The work reported herein focused on the effects of mechanical activation via ball-milling, and the environment of mill (air, N₂, CO₂) on the activity of coal fly ash as an aluminosilicate precursor in production of geopolymer (via alkali activation). N₂ was selected as an inert environment where reactions with the mill environment would not be a major factor. Air and CO₂ were considered as reactive environments that could affect the performance of the resultant (mechanically activated) coal fly ash.

Materials

The raw materials used in this process were landfilled coal ash: calcium oxide: basalt: sodium hydroxide at 82:6:6:6 weight ratios. The landfilled coal ash was obtained from local landfilled in Michigan; this ash had been landfilled for 2 years. Typical scanning electron microscope images of the landfilled coal ash are shown in Figure 1. The surface of landfilled ash is not smooth, which may be due to hydration and carbonation reactions during the period of disposal in landfill. The

chemical composition of landfilled coal ash is presented in Table 1. It is worth mentioning that basalt generally comprises SiO_2 , Al_2O_3 , CaO , FeO , MgO and TiO_2 , which are also found in the landfilled coal ash.

Sample	SiO_2	CaO	Fe_2O_3	Al_2O_3	SO_3	MgO	Na_2O	K_2O	BaO	TiO_2	SrO	P_2O_5	others
Landfilled ash	25.21	24.08	18.46	13.12	2.27	2.9	2.8	2.4	2.44	2.37	1.47	0.95	1.08

Table 1: Chemical composition of the landfilled coal ash (wt.%).

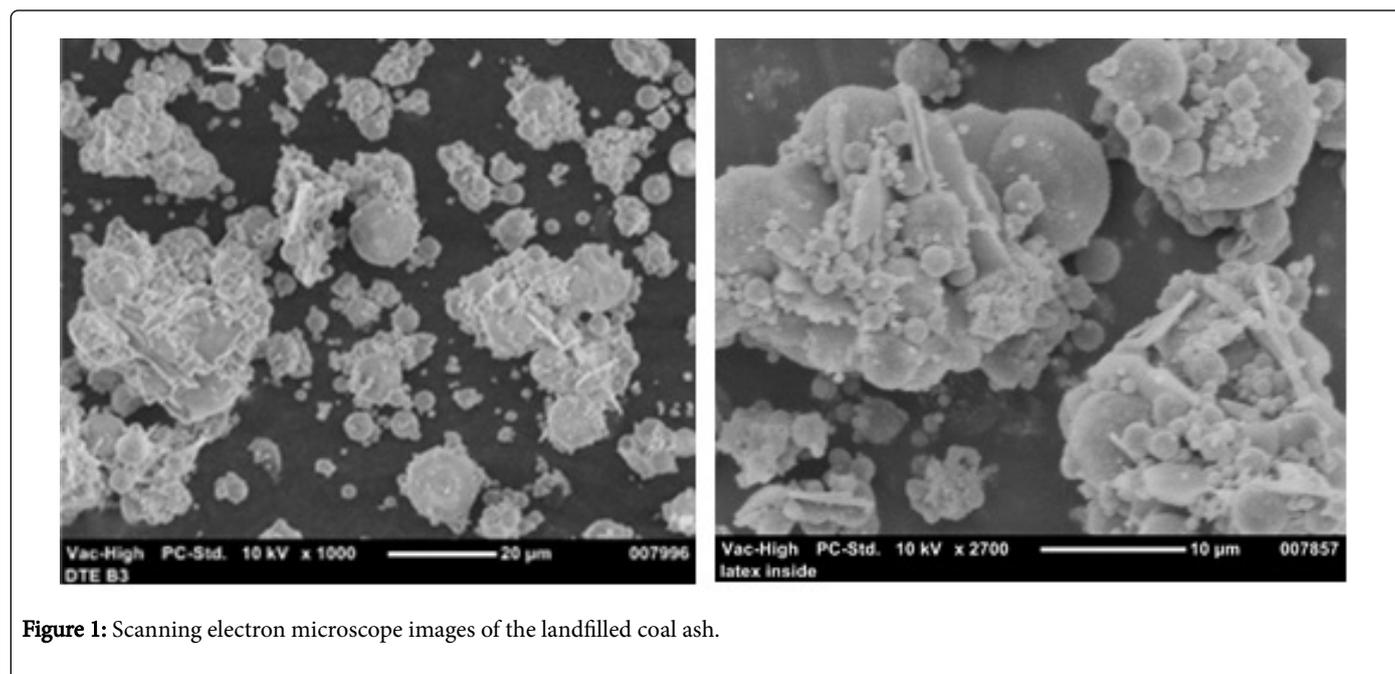


Figure 1: Scanning electron microscope images of the landfilled coal ash.

Methods

A ball mill with diameter of 140 mm and height of 140 mm, made of steel, was used at a rotational speed of 40 rpm to mill the geopolymer cement. At each time, 400 g of raw materials was milled with 4000 g of steel ball. The milling duration was 4 hours in each of the milling environments (air, N_2 and CO_2). Temperature at the mill surface were monitored using a temperature sensor with data storage capability.

The resulting geopolymer cements were evaluated via FTIR spectroscopy. For this purpose, 2 mg of cement was mixed with 200 mg of KBr, and the dry blend was formed into pellets using a high-pressure injection molding machine. A Jasco FT/IR-4100 spectrometer was used to perform these tests over a measurement range of $400\text{-}4000\text{ cm}^{-1}$.

The pH values of cements in solution were measured by dissolving 1 g of the geopolymer cement in 100 g of distilled water. The solution was placed on a shaker, and the initial pH values as well as those after 1 hour and 24 hours were measured. The total dissolved content (TDS) and electric conductivity of solutions were also measured in order to gain insight into the dissolution process of the hydraulic binder.

The heat of hydration of cements was measured using the calorimetry test method (ASTM C1679) using an I-cal 2000 HPC calorimeter manufactured by Calmetrix Inc. (Boston, USA). In this test, cement was mixed with water (by hand) at water/cement weight ratio of 0.40 for 30 seconds. The fresh paste was placed inside the

calorimeter, and the exothermic heat release was monitored over 24 hours.

A 20 Quart planetary mixer (Hobart A-200) was used to mix the mortar mixtures comprising cement, silica sand, water and super plasticizer. Mixing was performed over 3 minutes at medium speed. The resulting fresh mix was cast into 50 mm cube molds, and consolidated via external vibration. The water/cement and sand/cement ratios of mortar mixtures were 0.5 and 2.75, respectively; superplasticizer was used at 0.5% by weight of cement to raise the fresh mix workability. The specimens were demolded after 24 hours, sealed, and stored at $22 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ humidity. The compressive strength of the cubic test specimens was measured at 7 and 28 days of age per ASTM C109.

Results and Discussion

Temperature of the mill exterior surface

Figure 2 shows the powder temperature when geopolymer cement processing via milling was performed in CO_2 , in air and in N_2 environments. The presence of CO_2 is observed to induce an early temperature due to the frictional effects during impact of balls and particles [17], and also probably the formation of carbonates as a result of exothermic mechanochemical reactions of the carbon dioxide gas with alkaline earth metal, alkali metal and other constituents of the solid raw materials. Microstructural changes under impact could also

have thermal implications [18]. The peaks of powder temperature mill after about 3 hours in the presence of CO₂, and then starts to drop gradually. However the peak powder temperature is showed after 30 min in air milling. The trends in the exterior surface temperature development of the mill with the milling duration are quite different in the presence of nitrogen. There is actually a drop in temperature during the first 20 minutes of milling, after which the temperature starts to rise slowly and seems to reach a plateau at 110 min, and then strats to drop gradually. Compare to initial temperature, the peak temperature of powder during milling in CO₂, in air and in N₂ increase 5.8°C, 2.3°C and 1.8°C. While the eventual temperature rise can be explained by the frictional impact of balls and solid raw materials, microstructural changes and mechanochemical reactions, the initial drop in temperature could result from the evaporation of the water present in solid raw materials in the N₂ environment, combined with the reduced extent of (exothermic) mechanochemical reactions due to the inert nature of N₂.

The sharp contract between the powder temperature development during milling in CO₂ versus air points at the role played by CO₂ to enhance mechanochemical effects. A host of other phenomena also occur during milling that could be affected by the milling environment. Examples include comminution (particle size reduction) accompanied with formation of new surfaces, crystal deformation, defect formation, shear stresses buildup, reduction of crystallite size, aggregation of crystallites, local (and momentary) rise of temperature and pressure, phase transitions, amorphization, chemical bonds breakage, acceleration of diffusion processes [18].

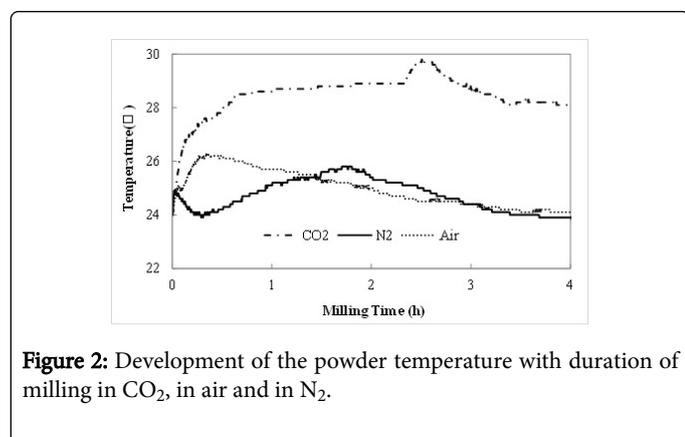


Figure 2: Development of the powder temperature with duration of milling in CO₂, in air and in N₂.

Specific surface area and morphology

As shown in Figure 3, the specific surface area of the geopolymers cement milled in air is the lowest, and that milled in CO₂ atmosphere is largest (1.19 times of that milled in air). The specific surface area of the geopolymers cement milled in N₂ is close to but still lower than that milled in CO₂. These results are similar to those reported by Rakhimov [19] and Kalinkina [15,20] where the specific surface area of slag geopolymers milled in CO₂ was found to be higher than that milled in air. After milling in air, a small amount of powder bonded to internal surface of the mill; this phenomenon was less pronounced when milling was performed in N₂, and it did not happen when milling was performed in CO₂. It should be noted that N₂ and CO₂ were input continuously from outside the mill; this was not the case when milling was performed in air. One may hypothesize that the gas flow (that was absent for milling in air) would enhance the dispersion of powder and thus the efficiency of the impact energy input to the powder. This effect

could be more pronounced in CO₂ with a density that is 1.5 times higher than that of N₂. These factors could influence the rise in specific surface area when milling was performed in N₂ and especially in CO₂.

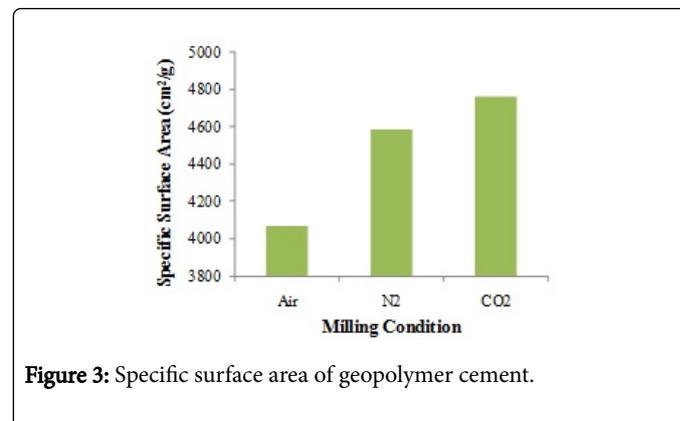
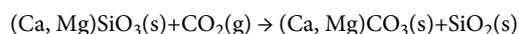


Figure 3: Specific surface area of geopolymers cement.

Scanning electron micrographs of geopolymers cements produced via milling in N₂, air and CO₂ are shown in Figure 4. These images suggest that the extent of mechanochemical reactions was probably the least when milling was performed in N₂, which could be explained by the inert nature of nitrogen that does not promote solid-gas reaction under input of impact energy. The reactive nature of air and CO₂ seem to produce morphological changes that could point at intense mechanochemical reactions. Reactions involving carbon dioxide and the silicate constituents of raw materials could be summarized as [21]:



This carbonation reaction could also destabilize the structure of silicates and promote other mechanochemical reactions.

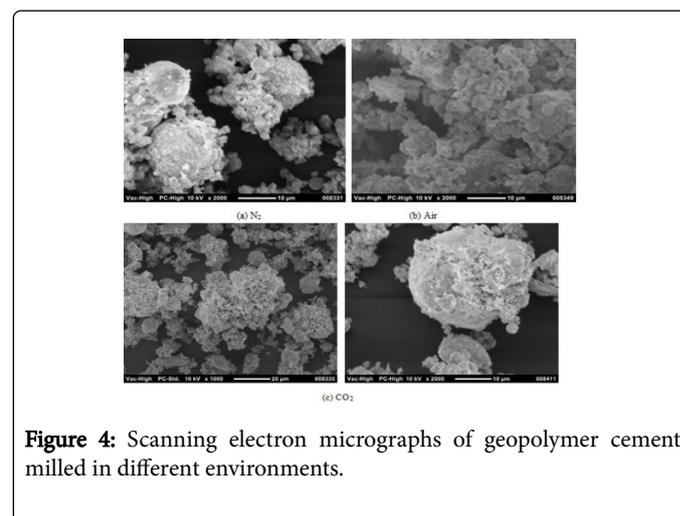


Figure 4: Scanning electron micrographs of geopolymers cement milled in different environments.

FTIR spectra

The FTIR spectra of geopolymers cement before and after milling in air, N₂ and CO₂ are presented in Figure 5. Before milling, the peaks at 1460 cm⁻¹ and 880 cm⁻¹ were attributed to the presence of carbonate on the surface [22-24] that form upon exposure of the raw materials to air. The peaks at about 3450 cm⁻¹ and 1650 cm⁻¹ can be attributed to the absorbed atmospheric water. The Si-O-Si stretching vibration produces the peak 985 and 1080 cm⁻¹, and the Si-(OH) stretching vibration produces the peak between 1094 and 1140 cm⁻¹ [25-28].

Peaks below 750 cm^{-1} can be attributed to M-O vibrations, where M is Al or Ca [23,29]. The band around 3640 cm^{-1} detected in all samples reflects the presence of sodium hydroxide. After mechanical activation, the band at 689 cm^{-1} is shifted to around 710 cm^{-1} , which points at the formation of new compounds via chemical reaction. The peak at 3640 cm^{-1} after milling is smaller than that before milling, which suggests that part of sodium hydroxide has been consumed in mechanochemical reactions.

After milling in CO_2 , the spectral peaks related to CO_3^{2-} of 2520 cm^{-1} , 1400 cm^{-1} and 870 cm^{-1} are sharper and more clear when compared with those observed after milling in air or in N_2 , which can be attributed to the mechanochemical carbonation reactions during milling. After CO_2 milling, bands appeared around 1663 cm^{-1} and 1622 cm^{-1} , and the band around 1640 cm^{-1} disappeared; a new band at 1921 cm^{-1} and the Si-O-Al vibration peak at 815 cm^{-1} [25] also appeared for the geopolymer cement processed via CO_2 milling. In the case of milling in N_2 , the peaks associated with water at 1640 cm^{-1} and 3400 cm^{-1} are relatively weak (compared to all other spectra), pointing at the greater loss of moisture during milling in N_2 . This phenomenon was relied upon earlier to explain the cooling effects observed when milling was performed in N_2 .

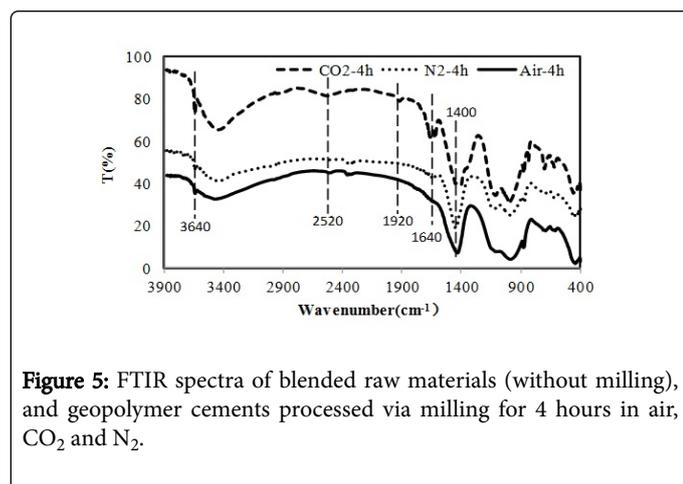


Figure 5: FTIR spectra of blended raw materials (without milling), and geopolymer cements processed via milling for 4 hours in air, CO_2 and N_2 .

pH, total dissolved solids and electrical conductivity in solution, and loss on ignition

The pH value of geopolymer cement (in solution) prior to and after milling in air, N_2 and CO_2 are shown in Figure 6. After milling in air and in N_2 , the pH value of geopolymer cement increased from 12.31 to 12.49. This can be interpreted as a rise in the activity of the blend of raw materials after mechanochemical transformation into geopolymer cement. Mechanochemical processing in CO_2 , on the other hand, reduced the pH value due to the formation of acidic carbonates. The highest pH value was obtained in N_2 , which could be due to some carbonation reactions when milling was performed in air. The total dissolved solids (TDS) increased (Figure 7) upon milling of raw materials in N_2 and in air, reflecting the greater activity of the mechanochemically processed geopolymer cement. The drop in TDS after milling in CO_2 can be attributed to the reduced solubility of the mechanochemically produced carbonates. The trends in electrical conductivity (Figure 8) are similar to those observed with pH and TDS test results, and can be explained similarly.

The LOI values (Figure 9) were highest after milling in CO_2 , and lowest after milling in N_2 . This observation could be attributed to the

mechanochemical formation of carbonated when milling was performed in air and especially in CO_2 .

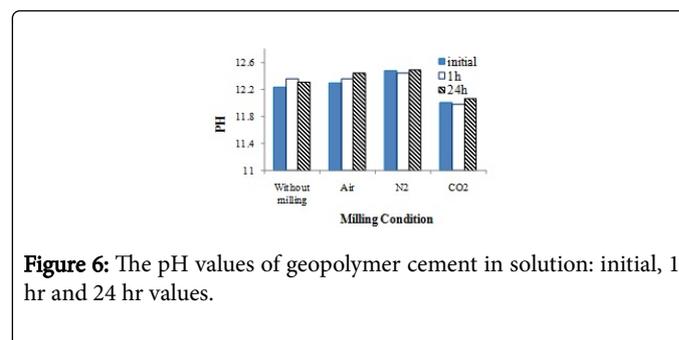


Figure 6: The pH values of geopolymer cement in solution: initial, 1 hr and 24 hr values.

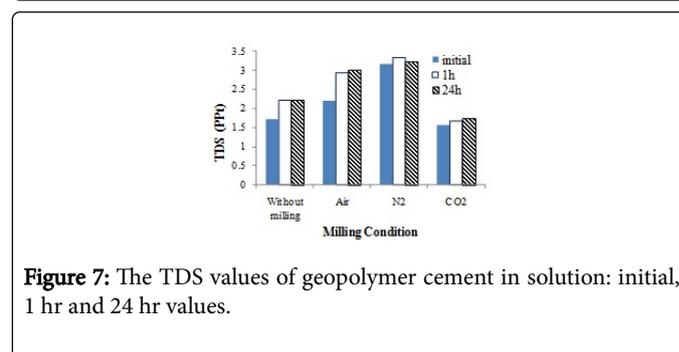


Figure 7: The TDS values of geopolymer cement in solution: initial, 1 hr and 24 hr values.

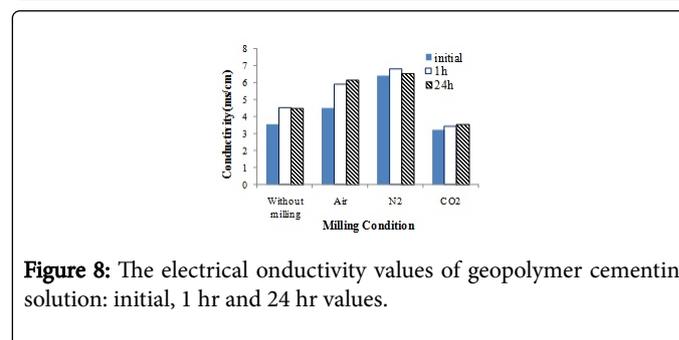


Figure 8: The electrical conductivity values of geopolymer cement in solution: initial, 1 hr and 24 hr values.

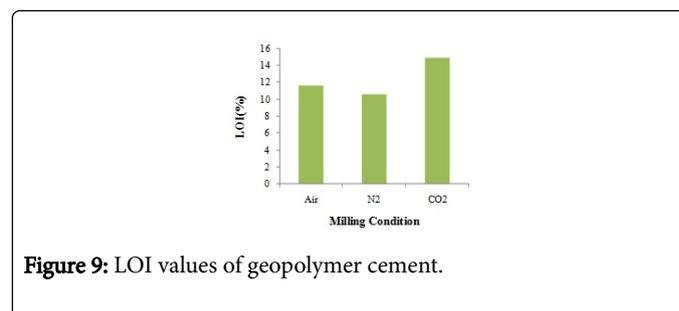


Figure 9: LOI values of geopolymer cement.

Heat of hydration

The rate and the cumulative heat release during hydration of geopolymer cements processed mechanochemically in air, N_2 and CO_2 are presented in Figure 10. After milling in N_2 and in air, the initial rates of heat release are higher, resulting in higher cumulative heat release. Milling in N_2 produced the highest total heat release. Both the rate and the cumulative heat release are the lowest for the geopolymer cement processed via milling in CO_2 . Geopolymer cements processed via milling in air and in N_2 exhibit only one exothermic peak after

about 2 minutes, while two peaks are observed after about 3.2 and 16.5 minutes for milling in CO₂. The mechanochemical effects of milling seem to have accelerated the rate of exothermic reactions [30,31]. This is indicative of the mechanical activation effects of milling. It has been reported [31] that the initial peak in hydration of geopolymer is related to the destruction of Ca-O, Mg-O, Si-O-Si, Al-O-Al and Al-O-Si bonds, and the second peak is due to the formation of Si-Al bonds. Higher pH values may be correlated with the higher rate of bond destruction that generates higher heats of hydration [32-34].

Due to carbonation, the pH value of geopolymer cement milled in CO₂ is the lowest. This lowers the dissolution of iron and the formation of Si-Al bonds, thus lowering the heat of hydration. It is possible that delayed formation of Si-Al bonds produces the second exothermic peak for the cement processed in CO₂. The pH value of the cement processed in N₂ is the highest, which can be used to explain its high rate and extent of heat release.

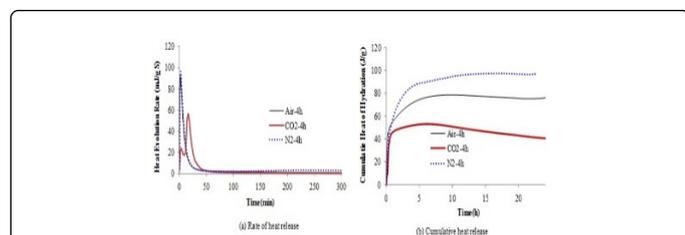


Figure 10: Heat of hydration test results for geopolymer cements processed via milling in different environments.

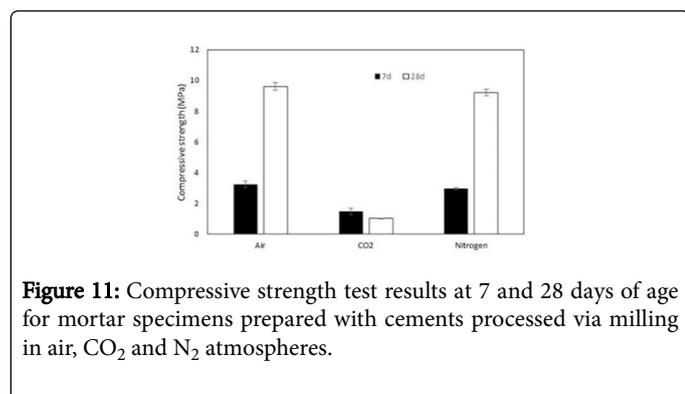


Figure 11: Compressive strength test results at 7 and 28 days of age for mortar specimens prepared with cements processed via milling in air, CO₂ and N₂ atmospheres.

Compressive strength

The compressive strength test results at 7 and 28 days of age are presented in Figure 11 for mortar mixtures prepared with different cements. Cements prepared via milling in air and in nitrogen produce comparable compressive strength values. The cement processed via milling in carbon dioxide, however, produced relatively low values of compressive strength. This could be attributed to the lower pH values obtained with the cement milled in carbon dioxide. This finding implies that carbon dioxide was captured by the cement milled in CO₂, and suggests that restoring the pH value of this cement by introduction of alkaline materials either prior to or after milling could feasibly raise the compressive strength obtained with this cement.

Conclusion

1. Landfilled ash when blended with basalt, CaO and NaOH produces a desired chemistry for production of a hydraulic cement. The blend of raw materials can be transformed into a hydraulic cement via input of mechanical energy.
2. The environment in which the blend of raw materials is transformed into a hydraulic cement via input of mechanical energy influences the nature of reactions and the end product properties. When input of mechanical energy (via ball-milling) was done in a CO₂ environment, the temperature measured on the mill surface increased initially, and then decreased. When milling was performed in N₂, on the other hand, temperature at the mill surface decreased with time. This could be partly due to exothermic reactions involving carbon dioxide during milling, that would not occur in an inert N₂ environment.
3. Milling in CO₂ environment transformed the calcium or magnesium silicates present in coal fly ash into carbonates. This seemed to cause release of smaller fly ash particles that are encapsulated in larger ash particles.
4. Input of mechanical energy activated the blend of raw materials. In an aqueous solution of the mechanochemically produced cement showed higher values of pH, total dissolved solids (TDS) and electric conductivity compared to that of blended raw materials. These values were lowest when milling was performed in CO₂ that can be explained by the carbonation reactions that take place when processing is performed in a CO₂ environment. Milling in air versus N₂ produced somewhat lower values of pH, TDS and conductivity in solution that could be explained by some carbonation that takes place in air.
5. The milling atmosphere affects the hydration heat of geopolymer cement. Due to mechano-chemical activation, the appearance of exothermic peak is appears earlier than that of previous test of without milling geopolymer. Milling in air and in nitrogen produced particularly high rates of heat release, and only one exothermic peak. Milling in CO₂, on the other hand, produced two peaks and lower rates of heat release. The cumulative heat release associated with hydration of the resultant cement was also smaller when milling was performed in CO₂. The relatively low rate and extent of heat release by the cement processed in CO₂ can be explained based on its low pH value in solution that delays formation of Si-Al bonds. Delayed formation of these bonds could explain the second exothermic heat release peak observed with the cement processed in CO₂. Processing in nitrogen, on the other hand, produces cements with relatively high pH values in solution. This accelerates the rate of hydration reactions and thus heat release.
6. The mortar compressive strengths produced with cements processed via milling in air and nitrogen were comparable. The cement milled in CO₂, however, produced relatively low compressive strengths. This was attributed to the reduced pH value of the cement milled in CO₂. The compressive strength obtained with this cement could be feasibly raised by increasing the alkali content of raw materials.

Acknowledgement

The authors are thankful to the U.S. Department of Energy for financial support of this investigation under Award No. DE-SC0015197.

References

- Mishra DP, Das SK (2013) Application of polymeric flocculant for enhancing settling of the pond ash particles and water drainage from hydraulically stowed pond ash. *Intern J Mini Sci Technol* 23: 21-26.
- Zand B (2009) An experimental investigation on liquefaction potential and post-liquefaction shear strength of impounded fly ash. *Fuel* 88: 1160-1166.
- Sushil S, Batra V (2006) Analysis of fly ash heavy metal content and disposal in three thermal power plants in India. *Fuel* 85: 2676-2679.
- Duxson P (2007) The role of inorganic polymer technology in the development of green concrete. *Cement Conc Res* 37: 1590-1597.
- Deventer V, Provis JL, Duxson P (2012) Technical and commercial progress in the adoption of geopolymer cement. *Minerals Eng* 29: 89-104.
- Palomo A, Grutzeck M, Blanco M (1999) Alkali-activated fly ashes: a cement for the future. *Cement Conc Res* 29: 1323-1329.
- Barbosa VF, MacKenzie KJ (2003) Thermal behaviour of inorganic geopolymers and composites derived from sodium polysialate. *Materials Res Bull* 38: 319-331.
- Mucsi G (2015) Control of geopolymer properties by grinding of land filled fly ash. *Intern J Min Process* 143: 50-58.
- Somna K (2011) NaOH-activated ground fly ash geopolymer cured at ambient temperature. *Fuel* 90: 2118-2124.
- Temuujin J, Williams RP, Riessen AV (2009) Effect of mechanical activation of fly ash on the properties of geopolymer cured at ambient temperature. *J Mat Process Technol* 209: 5276-5280.
- Balachandra AM (2017) Development of Refined Chemistries and Processing Methods for Integration of Carbon Dioxide into a Hydraulic Binder for Effective Heavy Metal Immobilization. *JOJ Material Sci* 2: 555-593.
- Aydn S, Karatay C, Baradan B (2010) The effect of grinding process on mechanical properties and alkali-silica reaction resistance of fly ash incorporated cement mortars. *Powder Technol* 197: 68-72.
- Kalinkin AM (2012) Geopolymerization behavior of Cu-Ni slag mechanically activated in air and in CO₂ atmosphere. *Intern J Min Process* 113: 101-106.
- Alex TC (2013) Utilization of zinc slag through geopolymerization: Influence of milling atmosphere. *Intern J Mineral Process* 123: 102-107.
- Kalinkina EV (2014) Binding properties of ferromagnesian slags after mechanical activation with alkaline-earth carbonates. *Inorganic Mat* 50: 1179-1184.
- Kalinkina E (2015) Interaction of magnesia-ferri ferrous slag with sodium hydroxide solutions: Experimental and physicochemical modeling. *Russian J App Chem* 88: 1127-1133.
- Takacs L, McHenry JS (2006) Temperature of the milling balls in shaker and planetary mills. *J Mat Sci* 41: 5246-5249.
- Ahmadian Baghbaderani H, Rahimpour MR, Delshad Chermahini M (2016) A combined experimental and modeling study of thermodynamics and kinetics of mechanochemical treatment for synthesis of Ni_{0.5}Co_{0.5}Fe₂O₄. *Mat Des* 95: 54-62.
- Rakhimova NR, Rakhimov RZ (2014) A review on alkali-activated slag cements incorporated with supplementary materials. *J Sustain Cem Based Mat* 3: 61-74.
- Kalinkin A (2013) Geopolymers Based on Mechanically Activated Non-Ferrous Slags. *Chem Sustain Develop* 6: 647-655.
- Montes-Hernandez G (2009) Mineral sequestration of CO₂ by aqueous carbonation of coal combustion fly-ash. *J Hazard Mater* 161: 1347-1354.
- Kalinkin A (2005) Chemical interaction of calcium oxide and calcium hydroxide with CO₂ during mechanical activation. *Inorg Mat* 41: 1073-1079.
- Qu J (2016) Effect of anion addition on the syntheses of Ca-Al layered double hydroxide via a two-step mechanochemical process. *App Clay Sci* 125: 267-270.
- Dharmal S (2013) Chemical Investigations of Some Commercial Samples of Calcium Based Ayurvedic Drug of Marine Origin: Kapardika Bhasma. *J Pharm Biol Sci* 6: 5-12.
- Barbosa VF, MacKenzie KJ, Thaumaturgo C (2000) Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers. *Intern J Inorg Mat* 2: 309-317.
- Bange JB, Patil LS, Gautam DK (2008) Growth and Characterization of SiO₂ films deposited by Flame Hydrolysis Deposition System for Photonic Device Application. *Progress Electromag Res* 3: 165-175.
- Swedlund PJ, Miskelly GM, McQuillan AJ (2009) An attenuated total reflectance IR study of silicic acid adsorbed onto a ferric oxyhydroxide surface. *Geochimica et Cosmochimica Acta* 73: 4199-4214.
- Gaggiano R (2013) An infrared spectroscopic study of sodium silicate adsorption on porous anodic alumina. *Surf Interf Anal* 45: 1098-1104.
- Puertas F, Fernández-Jiménez A (2003) Mineralogical and microstructural characterisation of alkali-activated fly ash/slag pastes. *Cement Concrete Compo* 25: 287-292.
- Ogino SI, Sato Y (2006) Relation of the number of cross-links and mechanical properties of multi-walled carbon nanotube films formed by a dehydration condensation reaction. *J Phy Chem* 110: 23159-23163.
- Pacheco-Torgal FJ, Gomes C, Jalali S (2008) Alkali-activated binders: A review: Part 1. Historical background, terminology, reaction mechanisms and hydration products. *Cons Build Mat* 22: 1305-1314.
- Fernández-Jiménez A (2006) The role played by the reactive alumina content in the alkaline activation of fly ashes. *Micropor Mesopo Mat* 91: 111-119.
- Petermann JC, Saeed A, Hammons MI (2010) Alkali-activated geopolymers: A literature Review. *App Res Assoc Inc*. Panama City, FL.
- Xie Z, Xi Y (2001) Hardening mechanisms of an alkaline-activated class F fly ash. *Cem Conc Res* 31: 1245-1249.