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CHARACTERIZATION OF FLUIDIZED BED FLY ASH FROM AMGALAN THERMAL STATION AND ITS APPLICABILITYFOR ALKALI ACTIVATED BINDER PREPARATION

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Geopolymer type paste has been prepared by alkali activation of circulating fluidized bed combustion fly ash (CFA). Ash residues of Baganuur lignite coal that used by Amgalan thermal station was applied as raw material. The particle size distribution, phase composition and chemical composition of CFA were examined and also used for alkali activated binder preparation. Geopolymerization products were characterized by mechanical testing, X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The highest compressive strength of the geopolymer type binder was 17.7(2.5) MPa.
Keywords*:* fluidized bed combustion fly ash, characterization, geopolymer paste, compressive strength.

1. Introduction

Fluidized bed combustion (FBC) is today a well established technology for generation of heat, power and a combination of these [1].

The Amgalan thermal station is located in Ulaanbaatar city and its construction started in August 2013 and was completed in April 2015. The Amgalan thermal station has been generating heat under trial conditions since September 2015. Amgalan thermal station will produce 388 megawatts of energy. The 388 megawatt (300 Gcal/h) supply is enough

power to support over 50 thousand households in the eastern district of Ulaanbaatar city [2]. The power plant has three boilers and expected to produce at least 50000 tonnes of CFA per annum and certainly will be caused environmental problems. Therefore, it is important to find a suitable way of utilization the CFA.

Generally, the ashes from the thermal power or thermal stations are either dumped for the landfill purposes or used in construction. One of the emerging applications of ashes in construction nowadays is the manufacture of so called geopolymers binders as an alternative to Portland cement. Geopolymer is an alkali-activated alumino- silicates which is able to produce a Si-O-Al framework, reacting at low temperatures. The name was given by Joseph Davidovits in 1970's [3].

Geopolymers have received considerable attention due to their excellent mechanical properties, low shrinkage, fire resistance, low energy consumption in building industry and engineering field [4-8]. They can be used for coatings and adhesives, new binders for fiber composites, waste encapsulation, and new cement for concrete [9-11]. Raw materials of geopolymers could be natural (alumino-silicate) minerals or industrial wastes such as fly ash [12-15], metakaolin [16-18], or slag [11,19,20], containing high concentrations of amorphous aluminosilicates.

Fly ash from lignite type coal contains a high calcium content and is classed as C-type, whereas bituminous and anthracite coals produce F-class fly ashes of low calcium but high silica and alumina content. Class F fly ash is considered to be more suitable for geopolymer formation and concrete production and is the most commonly used raw material for this purpose [21,22].

Because of relatively low combustion temperature (800-900 °C) CFA possesses different mineralogical content than that produced in the high temperature burning thermal power station, though, using of the same coals. Geopolymer type of concretes have been prepared by fly ashes of the 4th thermal power station of Ulaanbaatar city [23]. However, there never been any attempts to characterize and utilize CFA of the Amgalan thermal station. In this work, we characterized the CFA of Amgalan thermal station and studied geopolymerization behaviour of this fly ash.

2. Experimental procedure

2.1. Materials

CFA sample was collected from the Amgalan thermal station in March 2016. The station uses coal from the Baganuur deposit. Fly ash samples of used in this work were analyzed by XRF, their particle sizes

were determined using a sieve analysis (ASTM C136), their crystalline constituents were determined by XRD (Shimadzu, MAXima_X XRD-7000) andtheir specific surface area determined by BET analysis (Horiba, SA-9600). Differential thermo gravimetric analyzer (Hitachi, STA 7300) was used to measure the weight loss of geopolymer samples with temperature using corundum crucible in air atmosphere. FTIR measurements were made on samples suspended in KBr discs using a Shimadzu FTIR 8200PC spectrometer.

2.2. Sample preparation and testing

Samples of the fly ash were activated with 8, 10, 12 and 14 M sodium hydroxide solutions, as well as solutions containing a mixture of sodium hydroxide and sodium silicate. The sodium hydroxide solutions were prepared from 99% pure NaOH flakes and the sodium silicate solution, obtained locally from the company "JGB" LLC, was a viscous liquid with a Na_2O/ SiO_2 molar ratio of 3.2 and a density of 1.31 g/cm^3, according to company's data sheet.

The activated CFA pastes were placed in 20 mm cubic metal molds, wrapped in plastic and cured at 70 °C for 24 h, then demolded for mechanical testing. The samples were prepared in batches of six and the data presented here are the average of four samples. Hardjito and Rangan [22] report that alkaline solutions with a weight ratio of sodium silicate to sodium hydroxide solution equal to 2.5 produces the highest mechanical properties but the present experiments used a range of weight ratios of sodium silicate to NaOH.

The compressive strengths of the geopolymer pastes were measured using a Universal testing machine (Jinan, WDW-50). Water adsorption was determined from the weight difference between dry samples and those immersed for 30 min in boiling water. The skeletal density was determined from the weight and geometric volume.

3. Results and discussions

3.1. Characterization of CFA

Table 1 shows the chemical composition of the fly ash used in this study, and indicates that CFA contains low calcium and iron than that of produced Baganuur coal in the 4th TPS of Ulaanbaatar city [23]. Discrepancy may be caused by a mineralogical composition change of coal impurity with duration. On the basis of the combined content of SiO_2, Al_2O_3 and Fe_2O_3 of the fly ash, the Baganuur fly ash is class F, according to ASTM C618 classification. Fig.1 shows particle size grading curve of

the CFA. The particle size distribution and BET of the fly ash are shown in Table 2.

Table 1

Chemical composition of fly ash

Constituents	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Mn_3O_4	LOI
Weight (%)	64.2	15.85	6.17	6.27	1.35	0.07	2.3
Constituents	SO_3	K_2O	BaO	TiO_2	Na_2O	P_2O_5	
Weight (%)	0.9	1.05	0.11	0.55	0.35	0.08	

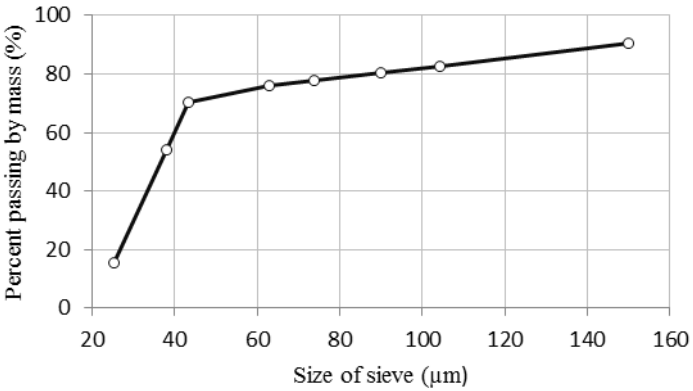

Fig.1. Grading curve of fly ash

Table 2

Specific surface area and particle size distribution of fly ash

Sample	BET (m^2/g)	D_{10}(μm)	D_{50}(μм)	D_{90}(μm)
CFA	4.88	16.45	35.2	149.1

The average particle size (D_{50}) and specific surface area of the CFAare a bit larger than the Baganuur fly ash from the 4th the TPS [23]. Thermal and XRD analyses of the CFA are shown in Fig.2 and Fig.3.

Raw CFA shows weight loss at about 500°C and it continues up to 640°C. The total weight loss of the CFA is 2.3% (Fig.2).

XRD pattern indicates (Fig.3) that the quartz (SiO_2) is the main crystalline constituent of raw CFA and calcite ($CaCO_3$), hematite (Fe_2O_3) and albite ($NaAlSi_3O_8$) exist as minor impurities. The presence of the calcite is an indication of a lower burning temperature of the fluidized bed combustion. Moreover, the glassy phase content is expected to be not much at fluidized bed combustion temperature (up to 970°C).

3.2. Alkali activated paste preparation

The compositions and mechanical properties of the geopolymer type paste are shown in Table 3. The compressive strengths of the samples increase with increasing alkali concentration, reflecting the increased solubility of the fly ashes. The inclusion of sodium silicate in the activating solution did not produce a noticeable improvement in the mechanical properties for samples prepared with between 8 and 14 M sodium hydroxide, except of using sodium hydroxide and sodium silicate weight ratio of 2:1. The highest compressive strength of 17.71 MPa was obtained when used alkaline solution consisting of 14M NaOH and sodium silicate with weight ratio of 2:1.

Table 3

Composition and mechanical properties of geopolymer pastes derived from CFA

Sample	NaOH	Na_2SiO_3(wt.)/ NaOH(wt.)	7 days		
			Water adsorption (%)	Density (g/cm^3)	Compress strength (MPa)
1	8M	1:0	27.03	1240.2	3.89
		1:1	24.67	1290.31	12.43
		1:2	28.7	1243.24	6.6
		3:1	25.53	1274.86	8.21
		2:1	24.8	1302.41	15.8
2	10M	1:0	25.4	1274.84	6.03
		2:1	24.44	1233.51	16.23
3	12M	1:0	21.44	1291.55	4.89
		2:1	22.41	1271.54	16.99
4	14M	1:0	19.16	1286.18	4.02
		2:1	24.7	1241.33	17.71
5	-	0:1	27.02	1178.56	5.0

The compressive strength change of samples prepared by using of 10 and 14 M NaOH and sodium hydroxide solution was 1.5 MPa which considered to be not much for the construction purpose. Therefore, for the economical reason was chosen 10 M NaOH and sodium silicate solution with weight ratio of 2:1 as activating solution for the further study.

3.3. Thermal analysis

Fig. 2 shows the thermo gravimetric analysis (TGA) of CFA and geopolymer paste. Weight loss of the geopolymer paste occurred up to 600 ^{o}C. Geopolymer contains free and structurally bonded water. There is a steep weight loss up to 180 ^{o}C. This weight loss is associated with evaporation of the free water. Weight loss between 200 ^{o}C to 600 ^{o}C was considered to be caused by structural water. The structural water was bonded in reaction product namely N-A-S-H gel. The total weight loss of the geopolymer was 9.6%. The geopolymer paste prepared from the fly ash was showed weight loss of 8% at 600^{o}C [24]. The 0.33% weight increase of the geopolymers was observed between 640 ^{o}C and 930 ^{o}C temperatures. It may related wth oxidation of the iron compounds that present in the CFA.

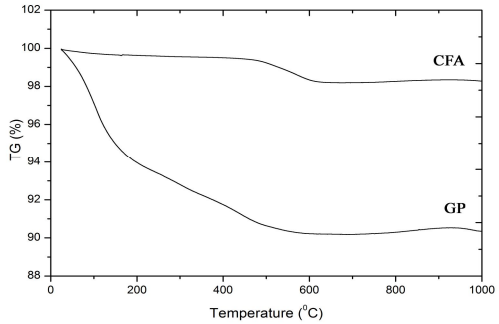

Fig.2. TG curves of the fly ash (CFA) and alkali activated material (GP)

3.4. Phase composition

Geopolymers are composed of either crystalline or non-crystalline (amorphous or glassy structure). Fig.2 shows XRD patterns of the alkali activated geopolymer paste and CFA.

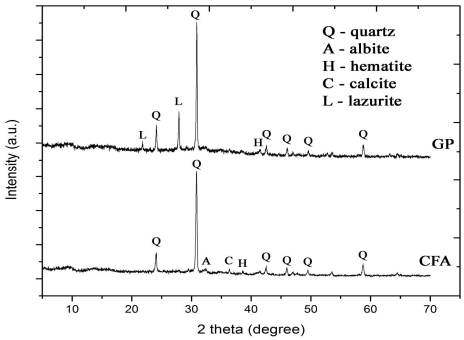

Fig.3. XRD patterns of the fly ash (CFA) and alkali activated material (GP)

Same as the CFA the geopolymer paste contains quartz (SiO_2) as the main crystalline component. However in the paste appear peaks of lazurite ($(Na,Ca)_8[(S,Cl,SO_4,OH)_2/(Al_6Si_6O_{24})$). The lazurite is a zeolite type compound belongs to the sodalite group. The broader hump appearing between 25° and 35° *(2θ)* is the characteristic feature of amorphous gels, mainly N-A-S-H gels. It can be suggested that the geopolymeric gel as well as zeolite type compound are contributing to increased compressive strength.

Fig. 3 shows the FTIR spectra of the CFA and alkali-activated geopolymer paste. Alkali activation produces some changes in the binding state of the CFA. Characteristic of FTIR bands of CFA and geopolymer product are shown in Table 4.

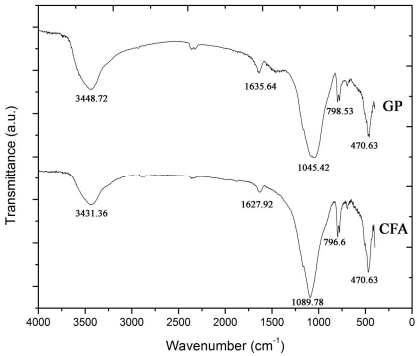

Fig.4. FTIR spectra of the fly ash (CFA) and alkali activated material (GP).

Table 4

Characteristic of FTIR bands of fly ash and geopolymer product

Wave number (cm^{-1})	Assignment
3500-3000	Stretching vibration (-OH, HOH)
1650-1620	Bending vibration (HOH)
1460-1420	Stretching vibration (O-C-O)
1090-990	Asymmetric stretching vibration (T-O-Si, T=Si or Al)
750-550	Symmetric stretching vibration (Si-O-Si and Al-O-Si)
470-460	Bending vibration (Si-O-Si and O-Si-O)

Some difference can be observed between FTIR spectrum of fly ash and geopolymer. The fly ash shows a broad band centered at 1090 cm^{-1}. It shifts to 1045 cm^{-1} upon alkali activation. Such shift of Si-O-Si asymmetric stretching vibration to a lower wave number is considered to be as indication of Al^{3+} into Si^{4+} sites with formation of Al-O-Si bond. This indicates that the formation of new product both the amorphous aluminosilicate gel phase and zeolitic type lazurite. The band in the region of 3500-3000cm^{-1} is assigned to stretching (-OH) and bending (H-O-H) vibration of water molecule.

4. Conclusion

Circulating fluidized bed combustion fly ash represents fine particle with average size of 35 □m and specific surface area of 4.88 m^2/g. Because of lower combustion temperature, the fly ash contains a little amount of non fully decomposed calcite. Alkali activated material prepared from the CFA shows the compressive strength of 16-17 MPa, at the best. The lower compressive strength of the geopolymers prepared from the CFA is likely to be caused lower content of glassy phase in this fly ash. However, it can be used for preparation of a low mechanical property building or road materials.

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ХАРАКТЕРИСТИКА ЛЕТУЧИХ ЗОЛ ИЗ АМГАЛАН ТЕПЛОВОЙ СТАНЦИИ, ОБРАЗОВАННЫХ В КОТЛАХ С КИПЕЩИМ СЛОЕМ. ВОЗМОЖНОСТЬ ИХ ИСПОЛЬЗОВАНИЯ ДЛЯ ПОЛУЧЕНИЯ ЩЕЛОЧНО АКТИВИРОВАННОГО ВЯЖУЩЕГО МАТЕРИАЛА

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Геополимерная паста была приготовлена щелочной активацией из летучих зол в циркулирующем кипящем слое. Летучие золы из бурого угля Баганурского месторождения, используемого на Амгалан тепловой станции, были выбраны в качестве сырья. Геополимерные материалы характеризованы механическими тестами, рентгенодифракционным методом, Фурье преобразованной ИК спектроскопией и термогравиметрическим анализом. Самая высокая прочность геополимерного соединительного материала составляет 17.7 (2.5) МПа.
Ключевые слова: летучие золы в кипящем слое, характеристика, геополимерная паста, прочность при сжатии.