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Utilization of Aluminium Dross as a Main Raw Material for Synthesis of Geopolymer

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Abstract

Aluminium dross contains both small particles and large agglomerates, where the recyclable part is the large agglomerates with high aluminium metal content. The residual Al dross is unrecyclable small particles with very low aluminium metal content. In this research, the residual Al dross from the aluminium recycle industry and the bagasse ash from a biomass power plant were used as main raw materials for geopolymer fabrication with alkaline solutions (Na_2SiO_3 and NaOH) using in the typical geopolymerization process. After mixing with alkaline solutions, the mixtures were uniaxially pressed into a cylinder die. The samples were cured for 3, 7, 14 and 28 days at the room temperature. The compressive strength and thermal conductivity of geopolymers were measured. In addition, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) was employed in order to study the microstructure and the structure change of the geopolymer products.

Key words: Aluminium dross; Bagasse ash; Geopolymer

Introduction

In construction, Portland cement has been used for a long time in the mixtures of concrete and mortar. However, the production of Portland cement requires very high energy to calcine the mixture of silica (SiO_2), alumina (Al_2O_3) and calcium carbonate ($CaCO_3$). This process emits carbon dioxide (CO_2), sulfur dioxide (SO_3), and nitrogen oxides (NO_X) gases causing the greenhouse effect and acid rain(1). Therefore, the researches on new materials for replacing cement have been carried out. One of the potential materials which could be used in this case is geopolymer. Geopolymer is a new class of synthetic aluminosilicate material formed by the reaction between aluminosilicate and alkaline activator so called geopolymerization process. Aluminosilicate materials are minerals composed mainly of silica and alumina. They can be found in natural materials such as clay, and also in industrial wastes such as fly ash, bagasse ash, oil palm ash and blast furnace slag, etc.

Solid waste from aluminium melting process with less than 45% Al metal is called “dross”. Dross may also be separated into “white dross” from primary smelters without salt cover and “black dross” from secondary smelter. The white dross comprised of fine powder from skimming the molten aluminium may contain 20% to 45% of recoverable metallic aluminium. Typically, black dross contains aluminium metal (10–20%), a salt-flux mixture (40–55%), and aluminium oxide (20–50%)(2). Although Al metal can be recovered from the white dross and the black dross, the non-recoverable dross is the byproduct classified as toxic and hazardous waste causing the problem to the disposal of dross. The aluminium dross contain both small particles with low aluminium content and large lumps with high aluminum content (20 to 30%). They can be separated by crushing, sieving and screening. The large lumps can be recycled whereas the small particles are non-recyclable and so called “residual Al-dross (AD)”.

Both Al-dross and AD consist mainly of alumina and silica, so they can be used as an additive for

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building materials. In the researches related to the use of Al-dross, it was found to be the material that could enhance the structural strengthening rate in calcium aluminate cement(3). Therefore, it is suitable for the applications requiring strength in the short time. Moreover, Al-dross can be used as a raw material in geopolymer reported by Saikrasun(4). The research showed that the synthetic of porous geopolymer could be produced using Al-dross as an inorganic foaming agent. The 1.5% of aluminum dross added porous geopolymer had a practical compressive strength. However, the use of Al-dross is only suitable for porous geopolymer with low compressive strength. Because of the relatively low amount of silica in the dross, it is not enough for the geopolymerization reaction. Aluminium nitride (AlN) and aluminium in Al-dross reacting with water producing ammonia gas and hydrogen gas(5). Moreover, the gases cause the uncontrollable shape (swelling). Therefore, it is necessary to find another raw material with high silica to react with Al-dross.

Bagasse ash (BA) is one of the most produced agricultural wastes in Thailand. Moreover, bagasse ash contains about 70 wt% silica and high porosity, which could be used as a source of silica for the geopolymerization reaction. It also absorbs gas generated by the reaction between the AD and the alkaline solution.

Therefore, this research focused on the utilization of AD and BA in Thailand for the geopolymer fabrication. The geopolymerization behavior and physical properties of the samples were studied according to the variation of AD:BA ratios and alkaline solution used in the process.

Materials and Experimental

Materials and Preparation of geopolymer

In the current study, geopolymers were produced from AD and BA in different condition. The AD was collected from secondary aluminium recycle plant in Thailand, and industry. The BA was sieved through the mesh number #18 (1,000 µm) prior mixing process. The particle size analysis of powders were carried out using laser particle size analyser (Mastersizers, Malvern, UK). The chemical compositions of calcined AD and as received BA were obtained by X-ray fluorescence (XRF). The XRD patterns of raw materials were obtained using X-ray diffractometer (Pananalytical X'Pert PRO).

In order to investigate the effects of AD:BA ratios on the properties of geopolymers, the mixtures with the AD:BA ratios of 0:100, 30:70, 40:60, 50:50 were produced using the unmilled AD and BA powders. The solid mixtures were mixed with alkaline solutions of Na_2SiO_3 and NaOH (10 M). The solid:liquid ratio used for all formulas was 4:1. The geopolymer samples were produced at various conditions as shown in Table 1. Then, the mixtures were uniaxially pressed into a cylinder die at the pressure of 2,200 psi. The cylinder samples were cured in the sealed plastic bags for 3, 7, 14 and 28 days at the room temperature.

Table 1. Conditions of the geopolymer samples.

Specimen label	Ratio		Na_2SiO_3 (wt%)	NaOH (wt%)
	Dross	Bagasse Ash (BA)		
BA(3:1)	-	100	3	1
BA(4:1)	-	100	4	1
30DB(3:1)	30	70	3	1
30DB(4:1)	30	70	4	1
40DB(3:1)	40	60	3	1
40DB(4:1)	40	60	4	1
50DB(3:1)	50	50	3	1
50DB(4:1)	50	50	4	1

The compressive strengths and density of geopolymers were investigated. Microstructure of geopolymer and the structural evolution of amorphous alumino-silicate were studied using scanning electron microscopy (SEM, JEOL JSM7800F) techniques and Fourier transform infrared spectroscopy (FT-IR Thermo Scientific, Nicolet 6700, U.S.A.), respectively.

Results and Discussion

Characterization of raw materials

The typical cumulative particle size distributions of AD and BA are given in Figure 1. The characteristic particle diameters of dross and bagasse ash were 15.51 µm and 25.12 µm, respectively.

The chemical composition shown in Table 2 indicates that the calcined AD consists of 66.5% alumina, 10% silica and 4.58% Na_2O, whereas the BA consists of higher silica content (70.4%), much lower alumina content (7.82%) and 9.14% calcium oxide. The XRD patterns of Al dross and bagasse ash are given in Figure 2. The phases of Al_2O_3, AlN, Al metal, $MgAl_2O_4$, NaCl, KCl, FeS_2 and $NaAl_2O_{17}$ were found in the AD. In addition, SiO_2 and $CaCO_3$ were found to be the main phases in BA.

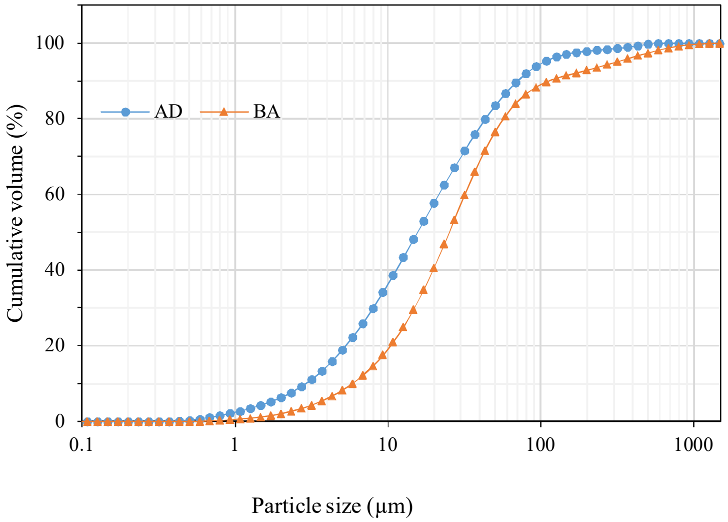

Figure 1. Cumulative particle size of AD and as received BA.

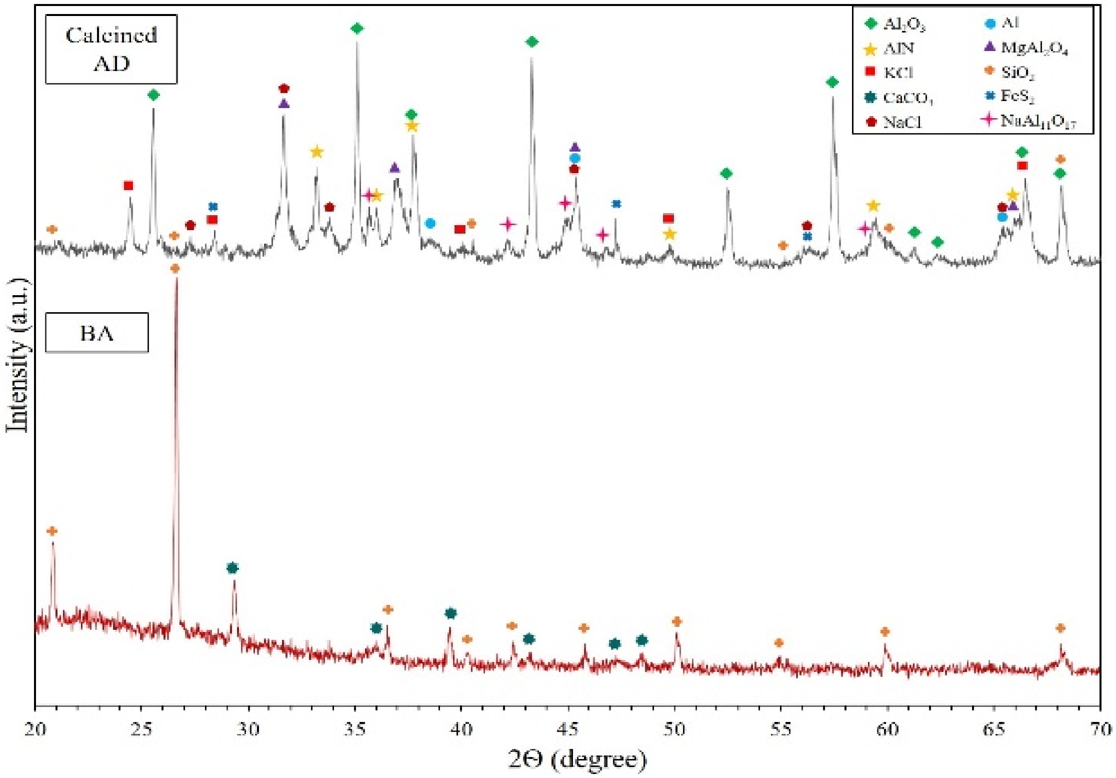

Figure 2. XRD patterns result for calcined AD and as received BA.

Table 2. Chemical composition of BA and calcined AD obtained by XRF technique.

Oxide basis	Calcined AD (%)	BA (%)
SiO_2	10	70.4
Al_2O_3	66.5	7.82
CaO	2.53	9.14
Fe_2O_3	1.12	4.68
K_2O	2.01	3.38
MgO	6.77	1.66
TiO_2	0.25	0.75
SO_3	0.5	0.38
Na_2O	4.58	0.12
Cl	4.4	0.09

Characterization of geopolymer samples

Compressive strength

The effects of alkaline solution on the compressive strength of geopolymer samples

The effects of alkaline solution on the compressive strength of geopolymer samples were presented in the Figure 3. The optimum proprotion of the alkaline solutions (Na_2SO_3: NaOH) was obtained for both geopolymer samples contained BA with and without AD. The ratio of Na_2SO_3: NaOH at 3:1 was found to be the best ratio for BA geopolymer sample without AD as the maximum strength could be obtained in this sample. The lower amount of NaOH in the alkaline solution (Na_2SiO_3:NaOH at 4:1) would not effectively dissolve Al and Si, and thus the condensation reaction might be completed$^{(6-7)}$. For the sample with BA and AD, the optimum Na_2SO_3:NaOH ratio was 4:1 since the strength of this sample was higher than the samples with Na_2SO_3:NaOH ratio of 3:1. Since the AD had low SiO_2 content, the Na_2SO_3:NaOH ratio of 4:1 gave rise to the increase of Si in the mixture, and helped developing the strength in this geopolymer sample.

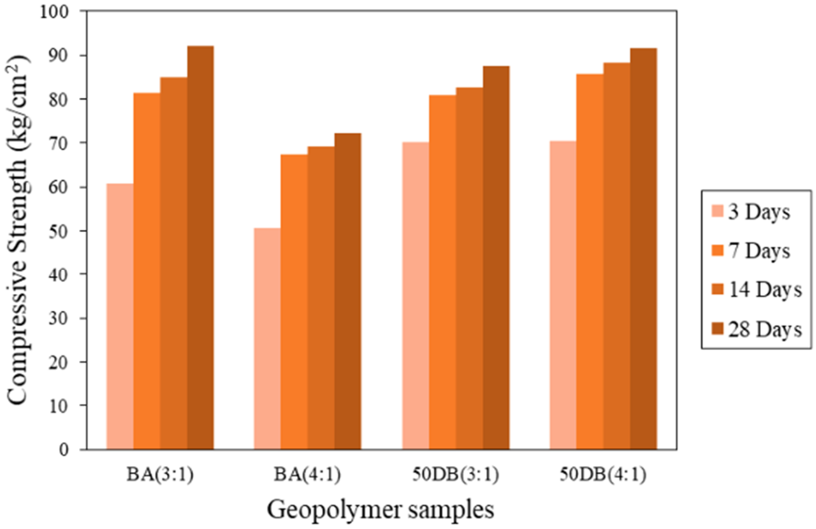

Figure 3. Compressive strength of the geopolymer samples curing for 3, 7, 14 and 28 day.

The effects of dross on compressive strength of geopolymer

Alkali activators are not the only factor affecting geopolymerization of compressed aluminosilicate materials. Because period of curing time, raw materials and the process of preparation also play a role in geopolymerization. The Figure 4 shows the variation of raw materials with the compressive strength and variation of curing time, the compressive strength of all samples have shown more than 70 kg/cm^2 and samples which are cured at 28 days have shown higher strength. The increase in the dross ratio at this range increased the compressive strength of the geopolymer. For the 28 day compressive strengths of geopolymers with dross 0, 30, 40 and 50 were 72.29, 84.62, 89.09 and 91.47 kg/cm^2, respectively. The optimum compressive strength was found in the 50DB (4:1) sample where the AD:BA was 50:50, and Na_2SiO_3:NaOH was 4:1.

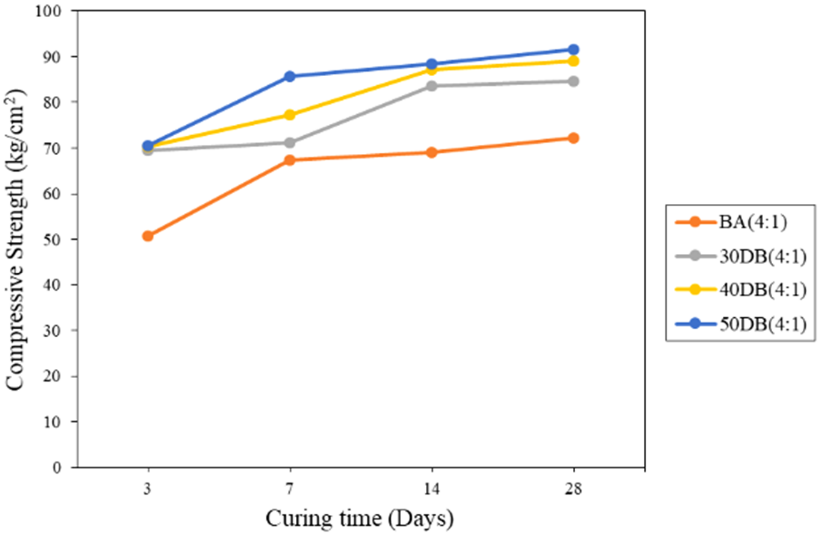

Figure 4. Plots of compressive strength as a function of curing time for geopolymer samples.

Density

The density of geopolymer samples with various AD:BA is presented in Figure 5. The density of geopolymer increased with the AD content due to the reduction of BA which has high porosity and low density. Thus, the samples with higher density could be obtained by adding higher amount of AD resulted in geopolymer samples with high compressive strength.

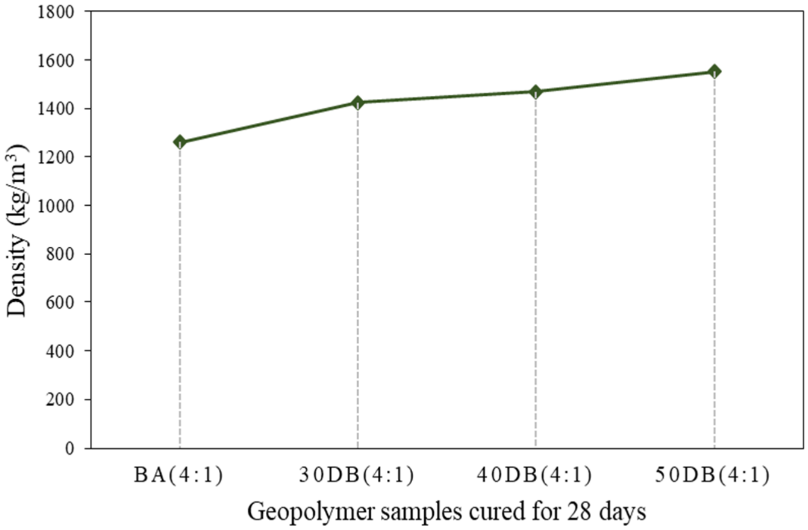

Figure 5. Plots of density of geopolymer samples cured for 28 days.

Microstructures

The difference in the microstructure of 50DB (4:1) and BA (4:1) geopolymer samples cured at 28 days can be clearly observed (Figure 6). In BA (4:1) sample, partially reacted area can be seen as a result of the gel formation causing the compactness. However, the unreacted area and the cracks can also be observed as shown in Figure 6(b). SEM images of 50DB (4:1) (Figure 6(c) and (d)) shows denser matrix comparing to the BA (4:1) sample indicating that AD could enhance the geopolymerization reaction in this sample. The results from this study show that Al dross can be used as a sustainable precursor for the development of geopolymer.

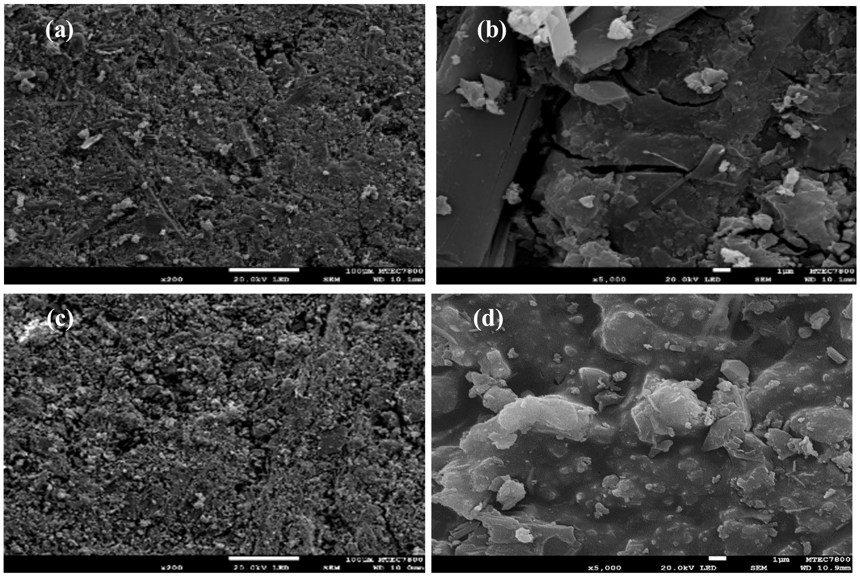

Figure 6. SEM of geopolymer sample cured for 28 days: (a) and (b) BA (4:1), (c) and (d) 50DB (4:1).

FTIR study

FTIR spectra of the raw materials and geopolymer samples are given in Figure 7 and Table 3. The difference between raw materials and geopolymer samples is the asymmetric stretching vibration of T-O-Si (T = Al, Si). For the BA and AD, this band appeared at 1,092 cm^{-1} and 1,088 cm^{-1}, respectively. However, this band shifted to the lower frequencies of 1,053 cm^{-1} for BA (4:1) and 1,045 cm^{-1} for 50DB (4:1). The shift is due to the partial replacement of SiO_4 tetrahedra of silicate network by AlO_4 tetrahedra, which decreases the length of silicate chain and leads to the formation of Al-rich geopolymer gel(8).

FTIR spectra of AD, BA and the geopolymers showing the strong characteristic peaks approximately 3,434-3,414 cm^{-1} and 1,643-1,621 cm^{-1} indicated the presence of water as they attributed to stretching and bending vibrations of hydroxyl, respectively. The band at 1,430-1,417 cm^{-1} represents the stretching vibration of O-C-O. The absorption band of calcium carbonate described by the stretching vibrations $\nu 2\text{-}CO_3^{-2}$ (876 cm^{-1}) was observed(9-10). The symmetric stretching vibrations of Si-O-Si and Al-O-Si were observed at the wave number of 800-500 cm^{-1}. The band at 704-696 cm^{-1} corresponding to the vibration of Al-O and Si-O tetrahedral. Additionally, the band at 465–459 cm^{-1} indicated the bending vibrations of Si-O-Si and O-Si-O (11-12).

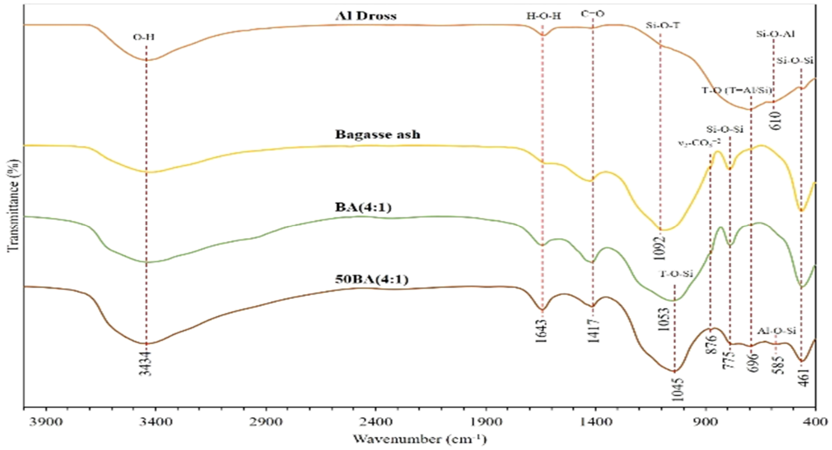

Figure 7. FT-IR spectras of raw materials and geopolymers.

Table 3. Characteristic of FTIR bands of raw materials and geopolymer sample.

Band	Assignments
3,434-3,414 cm^{-1}	Stretching vibration of OH
1,643-1,621 cm^{-1}	Bending vibration of H-O-H
1,430-1,417 cm^{-1}	Stretching vibration of C=O
1,092-1,045 cm^{-1}	Asymmetric stretching vibration of T-O-Si (T=Al, Si)
876 cm^{-1}	Stretching vibration of CO_3^{2-} ion
704-696 cm^{-1}	Vibration of tetrahedral T-O (T=Al, Si)
800-500 cm^{-1}	Stretching vibrations of Al-O-Si and Si-O-Si
465-459 cm^{-1}	Bending vibrations of Si-O-Si and O-Si-O

Conclusion

Based on the experimental results, the following conclusions can be drawn.

1. AD could be used as a main raw material incorporating with BA for the fabrication of geopolymer products.
2. The compressive strength of the samples increased with the higher amount of AD 50 wt% added to the sample.
3. The optimal ratio of the alkaline solution (Na_2SiO_3:NaOH) was 4:1 as this ratio had the adequate Na and Si for the geopolymerization reaction of AD and BA mixtures.
4. The addition of AD in the mixture encourage the geopolymerization reaction because the length of silicate chain decreased leading to the formation of Al-rich geopolymer gel.

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