INFLUENCE OF RED MUD ON THE PROPERTIES OF GEOPOLYMER DERIVED FROM MECHANICALLY ACTIVATED LIGNITE FLY ASH

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Abstract

The paper encompasses our studies on the co-utilisation of two major industrial waste materials of Hungary, lignite fly ash and red mud. Lignite fly ash, after mechanical activation for different duration has been characterised for particle size distribution and specific surface area. The red mud has been analysed for residual alkali content and together with the fly ash, for mineralogical phases. Geopolymerisation of fly ash has been carried out with various proportions of red mud ranging between 0–30 % by weight. The compressive strength of fly ash based geopolymer increased until a certain dosage of red mud and then decreased. Optimal red mud addition in fly ash geopolymer was determined. The influence of red mud on phase composition was determined by XRD analysis and FTIR studies.

Introduction

Fly ash is a pozzolanic finely dispersed residue (mineral matter showing pozzolanic activity) collected in electrostatic precipitators following combustion of coal in power plants. Particle size distribution of the fly ash depends on minero-genetic composition of the fuel coal, the fineness of grinding and parameters of the system the fly-ash was collected in. One of the limitations associated with lignite fly ash is the low reactivity which makes them less desirable for use in construction sector. Thus, to overcome this problem, the reactivity of fly ash can be increased by mechanical activation by grinding.[1,3,5]

Kumar and Kumar[2] investigated red mud, a residue of Bayer's process to be used synergistically with fly ash to develop geopolymer. An improvement in intensity of geopolymerisation was observed with the red mud addition at all replacement levels,

but improvement in setting time and compressive strength was observed only in the samples containing 5–20 % red mud.

Van Riessen et al.[7] examined various industrial residues to manufacture geopolymers. Geopolymers with a Si/Al ratio of 2.3 and a Na/Al ratio of 0.8 were targeted. With synthetic Al-plant spent liquor as the alkali activator, geopolymers with a mean compressive strength of 33 MPa were synthesised.

The goal of this paper is to reveal the effect of mechanical activation on geopolymer properties as well as to investigate the possibilities to replace the alkali activator and aluminosilicate by red mud.

Materials and Methods

Fly ash (FA) is originated from lignite based power station (Visonta, Hungary) and red mud (RM) was sampled from Almásfüzitő tailing (Hungary).

The particle size distribution of the raw and the ground materials was measured by HORIBA LA-950V2 laser diffraction particle size analyzer in wet mode using distilled water as dispersing media. The specific surface area (SSA) was calculated using PSD data by the laser sizer software. The red mud sample is characterised as much finer particle size distribution (x_{50}= 2 µm) than the fly ash sample (x_{50}= 49 µm).

Moisture content (n) of fly ash was very low 0.27 %, however that of the red mud was significantly higher 33.64 %.

The structure of the geopolymer product was investigated by FT-IR. Stretching and bending vibrations of chemical bonds in samples induced by infra range electromagnetic waves detected by JASCO FT-IR 4200 type Fourier Transformed Infrared Spectrometer in reflection mode, a diamond ATR was used.

The mineralogical composition was determined by a Bruker D8 Advance XRD powder diffractometer (Cu-Kα radiation, 40kV, 40mA) in parallel beam geometry (Göbel-mirror). Patterns were recorded in 2-70° (2θ) range, with 0.007° 2θ) steps in 42 seconds, obtained with Vantec-1 position sensitive detector (1° window opening). Phase identification was made by Search/Match (multiple iteration) on ICDD PDF2 (2005). Quantitative evaluation was made by Rietveld-refinement in TOPAS4 software, using FPM based instrumental convolution. Structural data originated from AMCSD database. The main mineral phases of fly ash were quartz, maghemite, hematite, anhydrite, albite and lime beside 52.5 wt% amorphous content. The

crystalline phases of red mud were hematite, cancrinite, gibbsite, calcite and lime with no amorphous content.

The residual alkali content of the red mud sample was analysed by titration of the aqueous extract. The result shows that 1 kg red mud contains 286 ml alkali with a concentration of 0.476 mol/l.

The mechanical activation experiments of fly ash were carried out in a conventional tumbling laboratory ball mill with the size of Ø303x305 mm internal diameter (smooth walled), with steel balls (max ball size 50 mm) as grinding media. The mill filling ratio of the grinding media was 30 V/V%, the material filling ratio was 110 V/V%. Residence time of mechanical activation was 5, 10, 20, 30 and 60 minutes.

Geopolymer specimens were made by mixing raw- or ground fly ash and NaOH solution using 0.67 liquid/solid ratio. Paste was placed to pre-oiled moulds and compacted by vibration. The compacted geopolymer paste was kept in mould for 24 hours insulated at ambient temperature, before removing the specimens. It is followed by heat curing at 90 °C for 6 hours. After heat curing the specimens were cooled down to ambient temperature. Mechanical tests were carried out by Compression Testing Machine at the age of 7 days.

Results and Discussion

Mechanical activation of fly ash

The primary effect of mechanical activation by grinding in our case was the particle size decrease and specific surface area increase. After 60 minutes grinding 11.6 µm median particle size was achieved from the initial value of 52.04 µm, indicating a 4.49 (r_{50}) size reduction ratio. Additionally, the "outer" specific surface area increase was significant, from 1152.07 cm^2/g it reached 5425.55 cm^2/g due to ball milling.[6]

Significant increase in the particle density was observed as function of grinding time. Namely, from the initial value of 1.94 g/cm^3 the density reaches 2.26 g/cm^3 after 20 min grinding time. It can be explained by the porous structure of fly ash, which by disaggregation will be turn into compact spherules by long term milling.

Geopolymer from mechanically activated fly ash

The effect of grinding fineness on geopolymer strength was investigated on specimens obtained using 6 M concentration NaOH solution. The geopolymer paste was prepared from 40 wt% alkaline activator (NaOH solution) and 60 wt% mechanically activated fly ash. The uniaxial compressive strength of the geopolymer

specimens was determined after 7 days of aging (Figure 1 a). The compressive strength increased from 2.6 MPa up to 6.5 MPa due to mechanical activation for 30 min grinding time. Furthermore, the 60 min ground fly ash based geopolymer was 21.5 % higher than that of the product consisting 30 min ground fly ash. The highest geopolymer compressive strength was 7.9 MPa using 6 M NaOH solution as alkaline activator and 60 min ground fly ash.

Fly ash - red mud based geopolymer

During the preparation of the geopolymer paste red mud was added in 5, 10, 15, 20, 25 and 30 % by mass for the dry mass of fly ash. Alkaline activator NaOH with 6 M concentration was used in different ratios depending on the workability of the paste. Namely for geopolymer paste containing 5 % red mud the activator was added in 40%, for that of 10, 15 and 20 %, the activator was added in 35 %, finally for 25 and 30 %, the NaOH solution was added in 30 %.

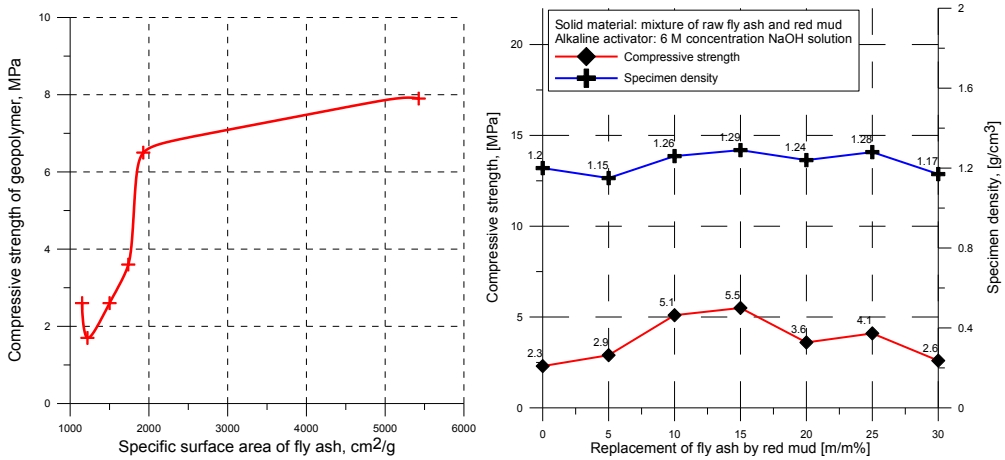

Figure 1: a) Effect of fly ash fineness on geopolymer compressive strength, b) Effect of red mud content on the geopolymer strength and density of specimen

The results of the experiments are shown in Figure 1b. Regarding the density of geopolymer specimens the values are fluctuating in the range of 1.15 and 1.29 g/cm^3. However, the strength values have a maximum point at 15 % red mud content, which was 5.5 MPa. Additionally, it can be observed that the characteristic red color of red mud will be dominant in the final product. It might be an advantage if commercialised product will be manufactured.

FT-IR spectra of geopolymer specimens containing red mud in different amounts can be seen in Figure 2. Peaks at 3390-3370 cm^{-1} are related to –OH, H-O-H bonds stretching vibration, at 1640 cm^{-1} corresponds to H-O-H bending vibration.

Peak at 1410-1425 cm^{-1} belongs to O-C-O stretching vibration of carbonate phase, which might be formed from remained unreacted activator solution and CO_2. Peaks at 1100-445 cm^{-1} related to Si-O-Si, Al-O-Si asymmetric and symmetric stretching and bending vibrations. As a result of red mud addition some peak (559 cm^{-1}) disappeared, while others (670, 612 cm^{-1}) appeared. It shows that slight differences in newly formed phases can be observed due to red mud addition. However, the most significant change was detected concerning the carbonate peak which was shifted from 1421 to 1414 cm^{-1}, at the same time the peak intensity decreased due to red mud addition indicating the change in the concentration of carbonate compounds.

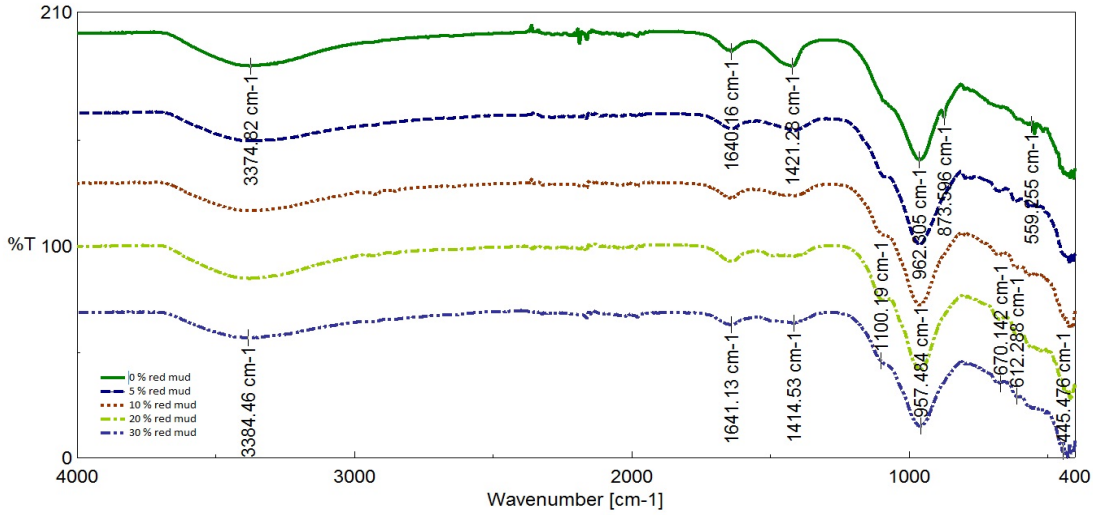

Figure 2: FTIR spectras of FA-RM based geopolymer

The changes in crystalline phase composition, by XRD, were influenced by both red mud and NaOH amount. Zeolite formation is observed, in low amounts, but also confirmed with our earlier evaluation process.[4]

Hydroxylcancrinite could be an anion substituted form of primary cancrinite from RM, in OH^- solution without reacting materials (lowest amorphous amount, Table 1). By increasing RM addition, cancrinite is formed, but the overall cancrinite+cancrnite-OH is reduced (-> dissolution and gel formation). Although amorphous content of geopolymers should decrease with RM addition (RM has no amorphous). However, the amount of amorphous was fluctuating between 33-28 %, only slight variation was detected. Zeolite formation is inhibited in the optimal 10 to 20 wt% RM addition, which resulted in the highest compressive strength of geopolymer specimens.

Table 1: Phase composition of FA-RM based geopolymers, in wt% (chemical formulas only orientative, given in the matching PDF files)

Phase Name chemical formula and its PDF file nr./RM %	0	5	10	20	30
Quartz SiO_2 PDF 46-1045	18.3	14.9	16.5	13.9	11.3
Albite $(Na,Ca)Al(Si,Al)_3O_8$ PDF 41-1480	8.8	6.6	9.5	7.5	3.9
Cancrinite-OH $Na_8(Al_6SiO_{24})(OH)_{1.4}(CO_3)_{0.3}(H_2O)_{6.35}$ PDF 88-1931		15.3	6.0	0.0	1.0
Faujasite-Na $K_{69.8}Al_{69.8}Si_{122.2}O_{384}$ PDF 26-0893	2.1	1.5	0.5	0.5	0.3
Calcit $CaCO_3$ PDF 05-0586	10.1	5.4	5.6	7.1	6.4
Hematite α-Fe_2O_3 PDF 33-0664	6.0	7.3	7.3	10.3	12.5
Maghemite γ-Fe_2O_3 PDF 39-1346	1.5	3.4	0.0	0.5	0.6
Akermanite-(Al) $Ca_2(Mg_{0.75}Al_{0.25})(Si_{1.75}Al_{0.25}O_7)$ PDF 79-2424	5.3	5.1	4.2	3.8	3.7
Magnesioferrite $(Mg_{0.146}Fe_{0.854})(Fe_{0.573}Mg_{0.427})_2O_4$ PDF 89-6187	4.9	1.3	5.6	5.1	4.3
Gobbinsite $Na_3Al_3Si_5O_{16}{\cdot}6H_2O$ PDF 25-0779	0.5	0.0	0.5	1.9	0.0
Thenardite Na_2SO_4 PDF 74-2036	2.9	1.6	2.5	3.7	4.0
Thermonatrite $Na_2CO_3{\cdot}H_2O$ PDF 08-0448	2.4	0.9	0.9	0.9	1.9
Microcline $K(AlSi_3)O_8$ PDF 76-1238	3.5	2.8	2.9	3.9	2.8
zeolite-LTA (or A) $Na_{12}Al_{12}Si_{12}O_{48}(H_2O)_{27}$ PDF 73-2340	0.6	0.9	0.1	0.2	0.1
Cancrinite $Na_6(Al_6Si_6O_{24})(CaCO_3)(H_2O)_2$ PDF 71-0776		4.3	5.0	11.3	13.6
Gibbsite α-$Al(OH)_3$ PDF 33-0018		0.8	0.9	0.3	1.6
amorphous	33.0	28.0	32.0	29.0	32.0

Conclusions

Based on the results of the laboratory investigation the following conclusions can be drawn down:

- Mechanical activation of fly ash tailored the properties of the resulted geopolymer.
- Red mud can replace the alkali activator and aluminosilicate phase in 10 – 15 %. Additionally, compressive strength increased due to red mud addition by 2.5 times.
- Phase composition changes are determined by RM and activator ratio, inhibits cancrinite and zeolites formation which lead to compressive strength increase.

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