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LUCYNA MADEJSKA*, ANDRZEJ JAROSIŃSKI**, SYLWESTER ŻELAZNY*,
MARIÁ KUŠNIEROVÁ***, MONIKA CHACHLOWSKA*

PROPERTIES OF GEOPOLYMER BINDER OBTAINED FROM FLY ASH

WŁAŚCIWOŚCI SPOIWA GEOPOLIMEROWEGO NA BAZIE POPIOŁU LOTNEGO

A b s t r a c t

Coal ashes from Kraków-Łęg Power Station were utilized during research. The purpose of this work was to obtain geopolymer as a result of polymerization reaction between aluminium silicates and potassium or sodium hydroxides. The following process parameters were tested: hardening conditions, influence of hydroxide concentration, and final product washability. X-ray diffraction analysis proved geopolymer formation, and further tests were performed, including mechanical resistance analysis as well as washability tests for heavy metals. Research results confirmed that the obtained geopolymer possesses resistance characteristics comparable to those of gypsum-anhydrite binders and can be used for building materials production.

Keywords: coal fly ash, geopolymers, heavy metals washability

S t r e s z c z e n i e

Popioły lotne użyte do badań pochodziły z Elektrociepłowni „Łęg" w Krakowie. Celem artykułu było otrzymanie geopolimeru – spoiwa tworzącego się w wyniku polimeryzacji zachodzącej z udziałem krzemianów glinu oraz wodorotlenków potasu lub sodu. Zbadano wpływ następujących parametrów: warunki reakcji, wpływ stężenia wodorotlenku oraz wymywalność końcową produktu. Potwierdzono utworzenie polimeru metodą dyfraktometryczną. Przeprowadzono także badanie wytrzymałości mechanicznej oraz wymywalności metali ciężkich. Wyniki badań potwierdziły, że uzyskany geopolimer ma właściwości wytrzymałościowe porównywalne ze spoiwami gipsowo-anhydrytowymi i może być wykorzystany do produkcji materiałów budowlanych.

Słowa kluczowe: popiół lotny, spoiwa geopolimerowe, wymywanie metali ciężkich

* PhD. Eng. Lucyna Madejska, PhD. Eng. Sylwester Żelazny, MSc. Eng. Monika Chachlowska, Institute of Inorganic Chemistry and Technology, Department of Chemical Engineering and Technology, Cracow University of Technology.

** Prof. PhD. Eng. Andrzej Jarosiński, Mineral and Energy Economy Research Institute, Polish Academy of Sciences.

*** Doc. PhD. Eng. Mariá Kušnierová, Institute of Geotechnics of the Slovak Academy of Sciences, Košice, Slovakia.

1. Introduction

The amount of coal fly ash from power plants is increasing and the problem has become a global one. Taking into account energetic, economic and environmental aspects, many research works have been undertaken, where coal fly ash is utilized as a starting material. Fly ash, although causing environmental pollution, is an important raw material for various applications. Many interesting methods of its utilization are proposed, for example removal of organic compounds due to adsorptive properties of fly ash; mine back fill, road sub-base, zeolite synthesis etc. Among these many possibilities of its utilization is building materials production (cement and concrete) as well as geopolymer formation- new alumino-silicate materials.

Geopolymers, known as inorganic polymers, were firstly developed by Davidovits in 1978 [1]. These materials are still attracting the world's attention because of their unusual properties. It is a class of three-dimensionally networked inorganic polymers, similar to natural zeolites. Unlike organic polymers, glass or ceramics, geopolymers are non-combustible, heat-resistant, fire and acid resistant. The geopolymerization reaction includes four steps:

1. The dissolution of alumino-silicate oxide in NaOH or KOH solution,
2. The diffusion of dissolved aluminium and silicon complexes from surfaces to the interparticle space,
3. The formation of a gel phase as a result of polymerization between silicate solution and Al and Si complexes,
4. Hardening of the gel phase by the exclusion of spare water to form final polymer product [2].

Starting materials play an important role in the geopolymer formation. Materials rich in silicon (like fly ash, slag) and materials rich in aluminium (kaolin clays, bentonites) were tested for geopolymerization. Fly ash as an important source material for geopolymers is available worldwide. It consists of finely divided ashes produced by burning different kinds of coal in power stations. The chemical composition of fly ash varies dependently on the mineral composition and CaO amount is the basis for fly ashes classification (F, CI and CH).

2. Materials and methods

Coal fly ash from Kraków-Łęg Power Station was used as a starting material in the experiments. Its chemical composition is presented in Tab. 1.

Main components in the tested initial material were SiO_2, Al_2O_3 and Fe_2O_3; their total amount was equal to 90 wt.% of the sample chemical composition. To determine the mineral composition of solid samples (initial material) X-ray diffraction on Phillips X'Pert diffractometer with graphite monochromator and CuK_α radiation was used. The washability of the solid product was defined according to PN-G-11011:1998.

The synthesis of geopolymer was conducted with coal fly ash and hydroxide solutions – NaOH and KOH that differ in concentration values, 10M and 16M, respectively. A hydroxide solution was slowly added to the fly ash sample at room temperature, then mixed for about 20 minutes. The final mixture was of gel consistency and it was mixed additionally for 10 minutes at the same temperature. After that the product was placed in a 4 × 4 × 16cm mould and vibrated for 5 minutes in order to release bubbles. The mould was set at 60°C for 120 hours, and later on seasoning was continued during 192 hours at room temperature.

After that time the mechanical strength of the samples was measured. Compressive strength tests for geopolymer samples in form of standard beams were carried out by compressive strength analysis apparatus ED-60.

Table 1

Composition of starting material – coal fly ash

Component	Wt. [%]
SiO_2	56.49
Al_2O_3	24.42
Fe_2O_3	9.01
CaO	0.69
MgO	3.13
Na_2O	2.06
K_2O	3.97
SO_3	0.52
TiO_2	0.79
P_2O_5	0.45

3. Results and discussion

The mineral composition of the tested initial material (coal fly ash) is presented in Fig. 1.

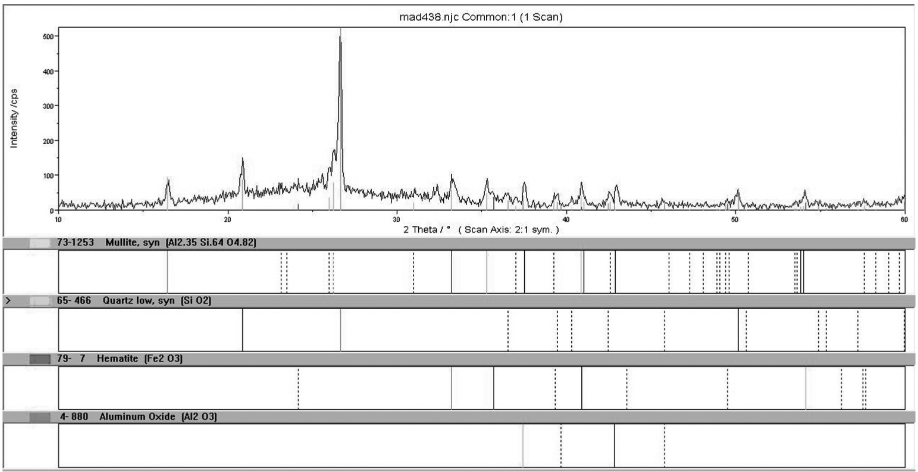

Fig. 1. XRD pattern of coal fly ash (from Kraków-Łęg Power Station)

Rys. 1. Dyfraktogram popiołu lotnego EC Łęg

On the basis of this analysis the following components were confirmed: quartz (SiO_2) as the main component, hematite and aluminium were observed in a form of two phases – Al_2O_3 and mullite.

Two experimental series were conducted. The first one concerned the influence of KOH concentration on mechanical properties of the final composite. The second series was carried out under the same conditions with NaOH solution. The experimental results are shown in Tab. 2.

Table 2

Compressive strength of final geopolymer product

Series number	Hydroxide	Concentration mole/dm^3	Compressive strength [MPa]
1	KOH	10.0	22.0
1	KOH	16.0	17.5
2	NaOH	10.0	26.5
2	NaOH	16.0	13.5

The obtained data indicate that the influence of the hydroxide concentration is essential on the compressive strength results. For example for 10M NaOH solution the compressive strength amounted to 26.5 MPa, the comparative results were obtained for 10M KOH solution: 22.0 MPa, respectively. The increase of the hydroxide concentration effects the decrease in compressive strength. The lowest compressive strength was obtained for 16M NaOH (13.5 MPa). From the above results one can assume that the compressive strength for geopolymer strongly depended on a kind of the hydroxide used, as well as its concentration.

An example of the mineral composition of the final geopolymer product is presented in Fig. 2.

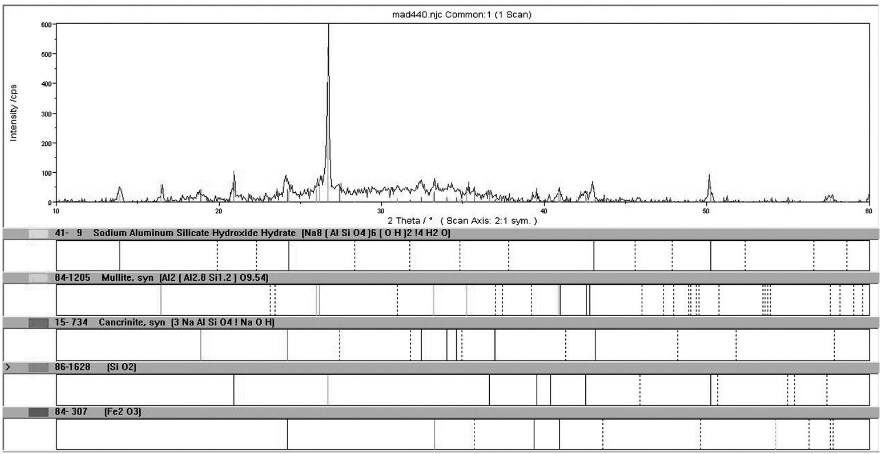

Fig. 2. XRD pattern of final composite

Rys. 2. Dyfraktogram kompozytu geopolimerowego

The presence of the following mineral phases was found in the samples: sodium aluminium silicate hydroxide hydrate (I), mullite (II), quartz (III) and hematite (IV). It can be stated that the first phase (I) from Fig.2. is responsible for geopolymer networking and as a consequence for binding and mechanical properties of the considered materials (composites).

The next stage of experiments was determining washability of heavy metals from the geopolymer product. The experimental procedure was conducted according to the Polish Standard [3] and the analytical results were obtained by means of Inductively Coupled Plasma Mass Spectrometry (ICP) method, using the Perkin-Elmer apparatus. The content of heavy metals in the leachate was compared with the initial values in the coal fly ash starting material. The results are shown in Table 3.

Table 3

Heavy metal content in leachate after washing

Component	Fly ash [ppm]	Leachate [ppm]
Cr	184	0.0108
Mn	852	0.0234
Pb	163	0.0141
Zn	295	0.0626
As	7	0.2372

Comparing the analytical results with the Polish Standard [3] it could be noted that the ICP analytical results do not exceed the standards for all tested elements.

4. Conclusions

Based on the results of tests described herein, the following conclusions can be drawn:
- the maximum compressive strength of the discussed geopolymer was reached for the experiments with the 10M NaOH solution,
- the increase of hydroxide concentration caused the decrease of geopolymer compressive strength,
- the kind of hydroxide used in the experiments (cation) affected the mechanical properties of the geopolymer,
- the composite formation was confirmed by XRD pattern,
- the compressive strength of the composite obtained in the experiments is satisfying and can be compared with high-quality gypsum and anhydrite binders,
- it should be pointed that the pH values during the washability test were about 11,
- the washability tests proved that the heavy metal content in the solution (leachate) does not exceed the Polish Standards, which means that all pollutants were immobilized in solid form.

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