

Utilization of Soda Ash Plant Solid Wastes in Production of Geopolymers

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Abstract — Soda ash plant in Lukavac (Bosnia and Herzegovina) generates significant quantities of different types of waste that are heavily burdening the environment. Fly ash and slag from the energy plant along with the waste filter brine from the soda plant represent the most important waste streams both in terms of quantity and level of environmental impact. Consequently, ongoing research is being carried out to find new ways of using these materials. The basic characteristics of flying ash, which may have an impact on its potential application, are: chemical composition, granulometric composition, specific gravity, specific surface, pozzolanic properties and radioactivity. In this research, the possibility of using solid waste, primarily fly ash from the energy plant, as well as the precipitate from the sediment pond I of „White Sea“ sediment basin in the production of geopolymer, has been investigated. The obtained results show that, by adjusting the ratio of these materials, geopolymers of satisfactory characteristics can be obtained, and that the initial composition of the mixture, determined by combining the proportion of individual raw materials, is extremely important for the preparation of geopolymers of appropriate physicochemical characteristics, using fly ash, precipitate from the “White Sea”, and water glass with NaOH and water, which are of particular importance.

Keywords — Fly Ash, White Sea Precipitate, Geopolymer, Alkaline Activation.

I. INTRODUCTION

Thermal power plants where pulverized coal is burned generate significant amounts of solid waste, primarily slag and fly ash. The fly ash particles range from 3-100 microns. Fly ash, depending on its composition, represents the material that needs to be appropriately disposed of [1]. If fly ash, according to its composition, does not belong to the class of hazardous waste, it should be treated as construction waste. This is the case with fly ash from SISECAM SODA LUKAVAC (SSL) soda factory. Disposal of this material is currently most often carried out by its addition to various cement composites, but also by using in the cement production process itself. The discovery of the geopolymerization reaction in aluminosilicate systems led to a large number of studies carried out in order to investigate the possibility of using fly ash, which also belongs to aluminosilicate systems, in formulations for obtaining geopolymers [2,3]. Research generally goes in two directions; examining the feasibility of utilization of fly ash in the synthesis of geopolymer and in determining or defining mechanisms of geopolymerization processes. Geopolymerization is the

reaction of solid aluminosilicate materials (natural or waste) with an alkaline solution, resulting in the formation of environmentally friendly inorganic polymers – geopolymers, which are characterized by good mechanical properties. For this reason, this paper examines the possibility of using fly ash from the SSL energy plant, which meets certain C class criteria, in the preparation of geopolymer, and the possibility of adding precipitate from the sediment basin “White Sea” into formulations for obtaining geopolymer.

II. THEORY

The “White Sea” sediment basin consists from four sediment ponds (I II III and IV) with total area of about 56 hectares. All technological wastewater from the Soda Factory is taken to the “White Sea” basin and contain mostly soluble matter (CaCl_2 , NaCl , Na_2SO_4) and suspended matter (CaCO_3 , CaSO_4 , $\text{Ca}(\text{OH})_2$, SiO_2 , MgCO_3 , Al_2O_3 and Fe_2O_3). The ash and slag from the steam and electricity generation process, hydraulic transport system, are dispatched to the “Black Sea” sediment basin located within the SSL factory area. There are four sediment ponds with a total surface area of 1.1 hectares. For the hydraulic transport of fly ash and slag into the “Black Sea” sediment basin, one uses the water for washing the lime on lime kilns that is acidic: pH 4-6. In this way, the neutralization of the overflow of the “Black Sea” is carried out. In the precipitate of the “Black Sea”, 70-80% is the ash, which can be used in the production of cement and thus achieve ecological and economic benefits. Fly ash is a pozzolanic material based on silicon, aluminum and calcium, which in combination with lime and water creates cement material with excellent properties. The ash density is $1,948 \text{ kg/m}^3$, and the bulk density is 640 kg/m^3 . Geopolymers denote a group of inorganic materials that can be synthesized from various raw materials such as calcined kaolin, fly ash, granulated slag, etc. [4], by reaction between the alkaline solution and the aluminosilicate feedstock. Geopolymerization is the reaction of solid aluminosilicate materials (natural or waste) with an alkaline solution, resulting in the formation of environmentally friendly inorganic polymers – geopolymers, which are characterized by good mechanical properties [5]. Two raw materials components are very important for the preparation of geopolymer, and these are the aluminosilicate raw material and alkaline activator of the geopolymerization process. The parameters that will depend on the reactivity of the raw material are: the

content of reactive silicon, the share of the amorphous phase, the particle size and the content of calcium.

III. EXPERIMENTAL

In order to investigate the possibility of using fly ash in the preparation of the geopolymer, the fly ash was characterized and compared with the literature requirements for materials that are intended to be used as raw materials [6] for obtaining geopolymer, and it can be summarized that:

- The share of silicon oxide and aluminum oxide together amounted to 51.43% of the total weight of fly ash. The desired ratio Si/Al is 2, and in the fly ash from the SSL were 2.17.
- The iron oxide content is preferably from 10 to 20 [wt. %] of the total mass, while in the ash used in this work this proportion amounted to about 9.00 [wt. %].
- The proportion of calcium oxide in ash from SSL was 11.40% which is higher than the requirements according to which it should not be greater than 5 [wt. %].
- Approximately 80% of fly ash particles should be smaller than 50 μm according to literature requirements. In the ash from SSL that was used to prepare geopolymer in this work, this share was 68.5%.

A. Material and Methods

Before determining the physicochemical characteristics, fly ash was dried in a drying oven at a temperature of

105°C to a constant weight. Determining the size and distribution of particle size was performed by the method of screening and diffraction of laser radiation on fly ash particles. The density of fly ash was determined by the pycnometer method. The method for determining the share of the reactive amorphous phase of flying ash was taken from [7] and was based on the selective dissolution of the fly ash sample in hydrofluoric acid. In accordance with numerous researches, scientific works dealing with the preparation of geopolymer [7,8,9] in this research too, as an alkaline activator for the geopolymerization process, a combination of sodium aqueous glass (AG) and NaOH has been used. The activator solution was prepared by mixing the predetermined components 24 hours before the preparation of the geopolymer itself.

For the purpose of analyzing and examining the effect of the alkaline activator/flying ash (AA/FA) ratio on the geopolymer's compressive strength, several geopolymer samples with different AA/FA ratios were made. For the purposes of the preparation of geopolymer in laboratory conditions, an additional amount of demineralized water was also used, which is necessary in order to achieve favorable flowability and workability of the system. For the preparation of the samples, 100 g of ash were used, as well as a mixture of ash and dry precipitate from "White Sea" (WS) of a total weight of 100 g. The used amounts of the individual components for the preparation of the geopolymer are shown in Table 1.

Table 1: The amounts of components used for the preparation of geopolymer

	Ash mass [g]	c (NaOH) [mol/l]	V (AG) [ml]	V (NaOH) [ml]	V _{sum} V _{vs} +V _{NaOH}	V (H ₂ O) [ml]	AA/FA
1	100,00	16	30,770	15,384	46,154	32	0,400
2	100,00	16	17,307	17,309	34,616	24	0,225
3	100,00	16	7,692	15,387	23,079	24	0,100
4	100,00	8	30,513	20,256	50,769	20	0,397
5	100,00	8	41,026	20,512	61,538	15	0,533
6	100,00	8	41,026	20,512	61,538	15	0,533
	90,00 FA						
7	+ 10,00 WS	10	23,462	23,462	46,924	15	0,305
8	100,00	8	46,026	25,512	61,538	20	0,598
	70,00 FA						
9	+ 30,00 WS	10	23,462	23,462	46,924	15	0,305

When the starting components are added to the system in the selected ratio, the mixture is stirred manually for 10 minutes.

After mixing, the resulting geopolymer mass is poured into PE containers, which are then closed with lids to prevent water loss due to hydrothermal activation. Each individual sample is compressed by shaking to minimize the porosity of the system and the better compaction. Samples were then conditioned for 24 hours at room temperature.

After that, hydrothermal activation was carried out, tempering the samples at a temperature of 85°C for 24 hours. After hydrothermal activation, the samples were

stored at room temperature until the moment of chemical, mineralogical and mechanical properties testing.

XRF Bruker diffractometer S8 Tiger and XRD Bruker diffractometer D4 Endeavor were used to record diffraction images of polycrystalline powder samples. Qualitative identification was performed using the appropriate database for inorganic compounds [12]. The diffraction images of polycrystalline samples of ash's dust were recorded in a wide angular region of 8-70° 2Theta, indicating that the fly ash, besides the crystalline, also contains a certain proportion of the amorphous phase.

IV. RESULTS AND DISCUSSION

The chemical analysis of fly ash from SSL showed that it contains 59.377 wt. % ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$) and 3.418% by weight of CaO, and – according to the American specification ASTM C618 [13] – it can be characterized as an ash satisfying the “C” criteria, i.e. ash with high content of CaO which is produced by combustion of coal of lower quality (brown coal and lignite), but not completely, because it has somewhat higher contents of CaO. Chemical analysis of precipitate from sediment pond I of “White Sea” is given in Table 2.

Table 2: Chemical composition of sediment pond I of “White Sea”

Component	Unit	Result
Ca(OH) ₂	%	5,0748
CaCl ₂	%	0,4990
Na ₂ CO ₃	%	0,8010
Na ₂ SO ₄	%	0,1496
CaSO ₄	%	1,1259
CaCO ₃	%	28,748
MgCO ₃	%	1,7093
Al ₂ O ₃	%	0,2041
Fe ₂ O ₃	%	0,3940
Net.+SiO ₂	%	0,6793
Water	%	56,8000

According to the obtained results, the precipitate from sediment pond I of the “White Sea” is characterized by high alkalinity, with a high content of calcium carbonate and calcium oxide, which is actually very convenient for the production of CSH gel (calcium silicate hydrate) which in certain proportions favorably affects the geopolymer structure, i.e. improves mechanical properties. The presence of heavy metals has not been determined in the test sample

The results of the granulometric composition of fly ash and the “White Sea” sediment are given in Tables 3 and 4.

It can be argued that both materials meet the requirements of ASTM C-618 standard [13] when it comes to sieve analysis, that is, the granulometric composition of fly ash as the main raw material for the production of geopolymer.

Table 3: Granulometric composition of fly ash

Class [μm]	Retained on sieve [%]	Retained on sieve [cum. %]	Passing through sieve [cum. %]
>500	31,496	7,576	92,424
250-500	47,336	39,072	60,928
125-250	10,156	86,408	13,592
75-125	2,408	96,564	3,436
45-75	1,028	98,972	1,028
<45	7,576	100	0
Σ	100		

Table 4: Granulometric composition of “White Sea” precipitate (dry part)

Class [μm]	Retained on sieve [%]	Retained on sieve [cum. %]	Passing through sieve [cum. %]
>500	8,35	5,01	94,99
250-500	39,04	13,36	86,64
125-250	18,14	52,40	47,60
75-125	27,89	70,54	29,46
45-75	1,57	98,43	1,57
<45	5,01	100	0
Σ	100		

The fly ash density is 2.2 g/cm³, satisfying the class "F", since it is lower than the density of fly ash "C" (2.6-2.7 g/cm³). The reactive share of the amorphous phase in fly ash, determined by the selective dissolution method in 1% HF, is 71.91% by weight, indicating the convenience of using the tested fly ash in the preparation of geopolymer. The obtained geopolymer samples were exposed to an open flame of 350°C, and there was no visual change of the sample, nor loss of its mechanical properties. To determine the degree of reacted fly ash in the homopolymer, a selective dissolution of the geopolymer samples in HCl was performed, with a concentration of 3 mol/l.

The stability of the geopolymer samples in an acidic medium was examined by treating them with 10% sulfuric acid (H₂SO₄) over a certain period of time. In this research, the finished geopolymers were treated 2 times for 5 days in 10% sulfuric acid. And after treatment of the sample for 10 days in 10% sulfuric acid, there are no significant degradations, nor changes in the sample of the geopolymer. During the course of the reaction, the sample was treated with phenolphthalein, with no change in color. In the treatment of the geopolymer sample in the acidic environment, the weight loss for the first sample was 16%, the other 12% and the third 16%. The loss of mass can be attributed to the time period to which the sample was exposed, as well as to the fact that there was evaporation of the water used to prepare 10% acid solution. The weight loss for cement materials is much higher under the same conditions and according to the available data it is even up to 41% [11].

Qualitative analysis of the diffraction images of polycrystalline samples of the powder of the geopolymer identified the crystalline phases present in the tested samples. Diffraction images of polycrystalline samples of fly ash dust taken in a wide angular region of 8-70° 2Theta indicate that fly ash, besides the crystalline, contains a certain proportion of the amorphous phase. From the XRD analysis and mineralogical composition of flying ash, it has been established that the main crystalline phases of flying ash are: magnetite, hematite and quartz (Table 5), while the main crystalline phases, determined by analysis of the diffraction patterns of the geopolymer sample, are: calcite, hematite and quartz (Table 6).

Table 5: Mineralogical composition of flying ash determined on XRD

	<i>Lime</i>	<i>Periclase</i>	<i>Anhydrite</i>	<i>Quartz</i>	<i>Mullite</i>	<i>Magnetite</i>	<i>Hematite</i>	<i>Calcite</i>	<i>Rutile</i>	<i>Fly ash Amorph</i>
%	CaO	MgO	CaSO ₄	SiO ₂	3Al ₂ O ₃ ·2SiO ₂	Fe ₃ O ₄	Fe ₂ O ₃	CaCO ₃	TiO ₂	
FA	2,84	1,14	7,99	9,37	2,07	7,75	9,96	0,05	0,19	54,02

Table 6: Mineralogical composition of geopolimer determined on XRD

<i>Geopolymer</i>	<i>Lime</i>	<i>Periclase</i>	<i>Anhydrite</i>	<i>Quartz</i>	<i>Mullite</i>	<i>Magnetite</i>	<i>Hematite</i>	<i>Calcite</i>	<i>Rutile</i>	<i>Fly ash Amorph</i>
%	CaO	MgO	CaSO ₄	SiO ₂	3Al ₂ O ₃ ·2SiO ₂	Fe ₃ O ₄	Fe ₂ O ₃	CaCO ₃	TiO ₂	
2	0	0,5	0	16,17	1,98	4,36	4,60	11,81	0,77	52,07
3	0	0,7	0	15,79	2,72	4,09	4,06	11,42	0,73	49,99
4	0	0,67	0	13,34	1,44	3,58	4,90	12,23	0,64	53,53
5	0	0,55	0	13,78	2,37	3,59	3,99	11,38	0,91	56,64
6	0	0,52	0	11,10	0,8	3,23	3,63	36,76	0,46	37,12
7	0	0,43	0	1,74	0	3,96	0,03	4,15	7,95	72,01
8	0	0,68	0	13,93	1,84	2,53	2,85	13,13	0,73	56,04
9	0	0,93	0	9,94	0,17	2,35	1,88	37,39	0,11	40,58

The chemical composition of the geopolimer determined on the diffractometer for the three selected samples of the geopolimer made is shown in Table 7.

Table 7: Chemical analysis of prepared samples of geopolymers

	<i>Sample 4</i>	<i>Sample 5</i>	<i>Sample 7</i>
SiO ₂ (%)	34,6660	37,2350	39,8360
Fe ₂ O ₃ (%)	11,8440	11,3702	12,1423
CaO (%)	16,0670	14,4380	13,2430
Al ₂ O ₃ (%)	10,8740	11,0270	12,2160
Na ₂ O (%)	8,5129	10,0561	8,9211
SO ₃ (%)	3,0424	3,5461	3,4457
MgO (%)	1,5939	1,6470	1,7512
K ₂ O (%)	1,0778	1,0327	1,0848
TiO ₂ (%)	0,5920	0,5932	0,6643
P ₂ O ₅ (%)	0,1191	0,0927	0,0856
MnO (%)	0,1311	0,1168	0,1363
NiO (%)	0,0914	0,0977	0,0967
SrO (%)	0,0763	0,0702	0,0883
Cr ₂ O ₃ (%)	0,0861	0,0622	0,0599
ZnO (%)	0,0148	0,0169	0,0132
Rb ₂ O (%)	0,0075	-	0,0086
CuO (%)	0,0145	0,0110	0,0170

Chemical analysis confirms the change of the original amorphous SiO₂ from fly ash. The results of the analysis of the diffraction patterns of the prepared samples further confirm that it is not only a structural transformation of the existing amorphous phase, but the formation of a new aluminosilicate amorphous phase (geopolymer) as a final product.

V. CONCLUSION

After investigations conducted during this research, it can be concluded that fly ash from an energy plant in SSL, although it has deviations from ASTM C-618 standards [13], (which is the base for determination of the quality of materials – ash – for use in the production of concrete, or geopolimer), according to its physicochemical properties, is a quality aluminosilicate material for the preparation of geopolimer. Similarly, the precipitate from the sediment pond I of “White Sea” in combination with fly ash at various ratios studied in this research is a usable material for use in the production of geopolimer, due to the fact that its composition contains CaO and Ca(OH)₂, which favor the creation of CSH gels that positively affect mechanical properties and, depending on the preparation of the sample, fill the cavities in a sample formed by evaporation of water due to hydrothermal activation. The reactive share of the amorphous phase in flying ash, determined by the selective dissolution method in 1% HF, is 71.91% by weight, which additionally points to the suitability of the application of the tested fly ash in the preparation of geopolimer. Using the X-ray diffraction on the polycrystalline samples of the prepared geopolimer, the formation of a new amorphous phase (geopolymer) is found in the diffraction angular region 2Theta = 25-38°. The existence of new crystalline phases in the prepared geopolymers has not been confirmed except that there has been a transition of CaO and CaSO₄ into CaCO₃ in finished geopolymers. The results of these investigations represent the basis at which additional tests should be carried out in order to accurately determine the optimal ratio of these components that will give geopolymers with characteristics (mechanical properties, thermal stability, freezing resistance, and atmospheric conditions) that

satisfy their application in specific areas or for specific purposes

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