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THE SYNTHESIS OF ZEOLITES FROM SEWAGE SLUDGE ASH

SYNTEZA ZEOLITÓW Z POPIOŁÓW Z OSADÓW ŚCIEKOWYCH

Abstract: The chemical composition of sewage sludge ash is similar to the chemical composition of substrates used for the synthesis of zeolites. The study shows the results of sewage sludge ash zeolitization with a fusion method. The research on sewage sludge ash before and after the process of zeolitization included the identification of a phase composition (XRD method) as well as the evaluation of both grain structure change (SEM method) and the cation exchange capacity (a method with the use of ammonium acetate). After zeolitization, sewage sludge ash contained hydroxysodalite, zeolite X and hydroxycancrinite. It was stated that zeolitization caused a positive increase of the cation exchange capacity.

Keywords: sewage sludge ash, zeolitization, hydroxysodalite, hydroxycancrinite, zeolite X, cation exchange capacity

Introduction

Utilization of municipal sewage sludge ash is an important issue in the current situation of the increase of the amount of incinerated sewage sludge [1, 2]. There are known methods of sewage sludge ash utilization in the production of lightweight aggregates [3, 4], bricks [5], mortars [6] and concrete [7]. A wide range of applications of sewage sludge ash in the production of building materials is the consequence of its chemical composition. Main components of sewage sludge ash are SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and P_2O_5 [8].

Zeolites are hydrated alumina silicates. The structures of zeolites consists of primary building blocks of inorganic tetrahedrons of silicon and alumina oxides. These atoms are strongly bonded together via oxygen bridges to form well-defined channels and cavities [9]. In the tetrahedral framework of synthetic zeolites other ions can also be found. Synthetic zeolites are obtained mainly under hydrothermal conditions with the use of various silica carriers in the presence of alkaline solutions [10]. For the synthesis of zeolites, coal fly ash [11] and paper sludge ash [12] can be used. The effect of the synthesis of zeolites depends among others on the activation temperature, the crystallization temperature, the crystallization time and the ratio of ash to sodium hydroxide. Besides, the ratio of Si:Al determines the formation of a particular type of zeolite [13, 14]. Due to zeolite properties such as high ion exchange, catalysis, adsorption and hydrothermal stability, they are widely used in environmental engineering, construction industry, refinery industry and agriculture [15-18].

The aim of the study was the verification of the thesis: the source of silica for the synthesis of zeolites can be sewage sludge ash. The research also covered the evaluation of the influence of zeolitization parameters on the ion-exchange properties of products.

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Material and methods

In this study, sewage sludge ash was obtained as a result of sewage sludge combustion in a laboratory furnace. The sewage sludge used in the study was taken from a municipal wastewater treatment plant in Sitkowka-Nowiny near Kielce. The sewage sludge was dried in a laboratory drier at the temperature of 105°C within 24 hours. Then, it was crushed in a mortar to a fraction < 125 µm. The sewage sludge was incinerated at the temperature of 980°C within 11 minutes. After the combustion, the sample remained in the furnace until it cooled down to the temperature of 20°C.

The chemical compositions of sewage sludge and sewage sludge ash were determined by using the X-ray fluorescence spectroscopy. Phase analysis of sewage sludge ash and sewage sludge ash after the zeolitization was performed with X-ray diffraction (XRD). The structure of the synthesized materials was observed by the scanning electron microscopy (SEM). The cation exchange capacity (CEC) was determined by a method with the use of ammonium acetate [19]. The concentration of ammonium in solutions was determined by the ion chromatograph.

Zeolitization of sewage sludge ash

Sewage sludge ash particles in the amount of 10 g were mixed and ground with granular NaOH to obtain a homogeneous mixture. The mixture was heated in an laboratory furnace at the temperature of 550°C for 1 hour. Different ratios of sewage sludge ash to NaOH samples were used to explore the effect of this parameter on zeolitization.

Table 1

Experimental conditions of sewage sludge ash zeolitization

Sample	SSA:NaOH	Activation temperature	Crystallization temperature	
			Time 6 h	Time 72 h
	[g/g]	[°C]	[°C]	[°C]
S1	1:1.4	60	60	-
S2	1:1.4	60	90	-
S3	1:1.4	90	60	-
S4	1:1.4	90	90	-
S5	1:1.4	60	-	60
S6	1:1.4	60	-	90
S7	1:1.4	90	-	60
S8	1:1.4	90	-	90
S9	1:1.8	60	60	-
S10	1:1.8	60	90	-
S11	1:1.8	90	60	-
S12	1:1.8	90	90	-
S13	1:1.8	60	-	60
S14	1:1.8	60	-	90
S15	1:1.8	90	-	60
S16	1:1.8	90	-	90

The sintered mixture was ground and mixed with distilled water (the applied concentration 3 N NaOH), followed by an aging process with an agitation in a shaking water bath at given temperatures of 60 and 90°C respectively. Then the mixture was crystallized under static conditions at the given temperature. After the completion of the crystallization, the solid product was washed with distilled water until the pH of the solution reached 10.0, then dried at 105°C for 10 hours. The synthesis conditions for each sample are shown in Table 1.

Results and discussion

Table 2 shows the characteristics of sewage sludge and sewage sludge ash. Sewage sludge ash has a high-silica content because of the SiO_2 to Al_2O_3 ratio of 3.74.

Table 2

Characteristics of sewage sludge and sewage sludge ash

Parameter	Units	Sewage sludge	Sewage sludge ash
pH	-	7.50	-
moisture	[%]	72.60	-
SiO_2	[%]	8.81	26.10
Al_2O_3	[%]	2.11	6.98
Fe_2O_3	[%]	3.74	12.40
CaO	[%]	5.66	18.50
MgO	[%]	1.42	4.56
SO_3	[%]	0.01	0.57
K_2O	[%]	0.58	1.98
Na_2O	[%]	0.16	0.60
P_2O_5	[%]	7.06	25.30
TiO_2	[%]	0.32	0.98
Mn_2O_3	[%]	0.03	0.11
SrO	[%]	0.02	0.06
ZnO	[%]	0.03	0.35
BaO	[%]	0.04	0,12
CuO	[%]	0.02	0.07
TOC	[% m/m]*	33.69	0.03

* a percentage by mass

Sewage sludge ash contains the following phases: amorphous substance - 13.61% m/m (a percentage by mass), quartz - 15.44% m/m, potassium feldspar - 4.96% m/m, whitlockite - 34.19% m/m, hematite - 10.76% m/m, stanfieldite - 13.05% m/m, tridymite - 7.99% m/m.

The XRD diffractograms of samples are presented in Figures 1 and 2. Sample S1 is defined by the absence of zeolites while the obtained phase was exclusively apatite. Samples S2-S4 are characterized by the presence of apatite and hydroxysodalite. They were subjected to a higher temperature of activation and/or crystallization in comparison to samples S1.

Hydroxysodalite is made of a cubic array of β-cages and exhibits a similar structure of sodalite [20]. The pore size of hydoxysodalite is smaller than of the zeolites with an eight membered ring aperture, e.g. NaA zeolite. Such a feature makes them an interesting material for the separation of small molecules like H_2 from liquid mixtures [21]. The structures of hydroxysodalite containing water can be dewatered. However, when the water molecule of the hydroxy-group leaves the sodalite framework at the temperature of above 600-700°C, the structure collapses. This process is irreversible and the resulting powder can no longer adsorb water. Therefore, hydroxysodalite is not thermally stable [22].

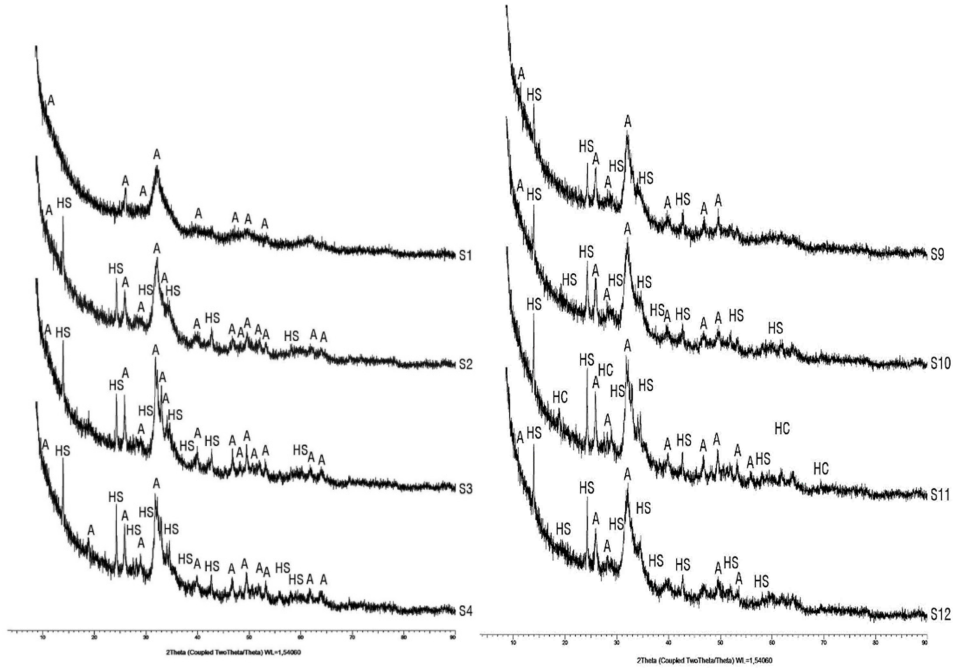

Fig. 1. XRD of sewage sludge ash after zeolitization by 6-hour crystallization

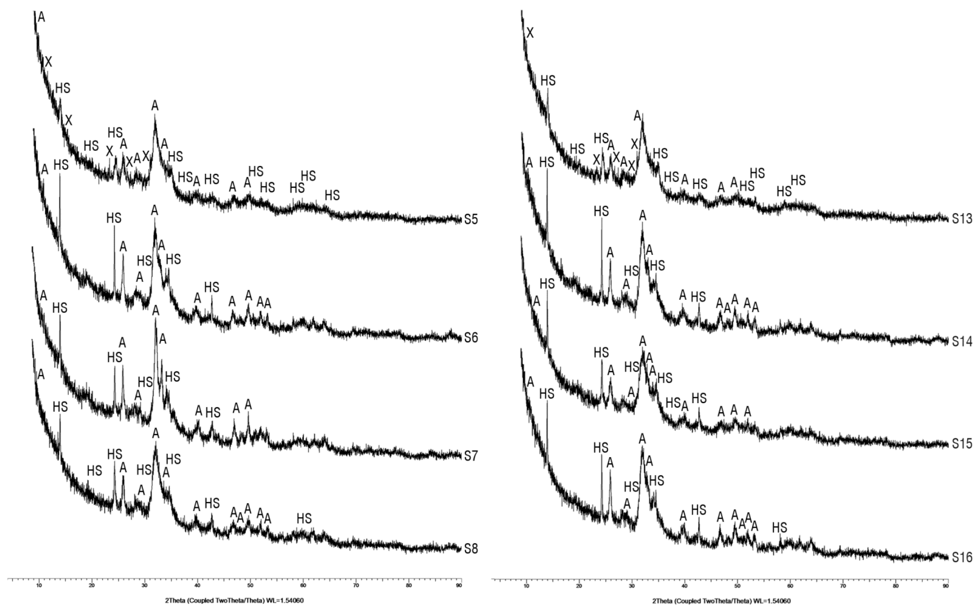

Fig. 2. XRD of sewage sludge ash after zeolitization by 72-hour crystallization

Zeolite X, hydroxysodalite and apatite were present in samples S5, that is in the samples of a 72-hour crystallization time and the SSA:NAOH ratio of 1:1,4. Zeolite X is a member of the faujasite group. Its structure is made up of a framework of 4-, 6- and 12-membered rings of SiO_4 and AlO_4 tetrahedra [23].

Zeolite X is the most difficult to prepare in high purity. This could be due to the thermodynamically metastable characteristics of highly porous faujasite [24]. Furthermore, zeolite X has a large pore size (7.3 Å) and a high CEC (500 meq/100 g) which make this zeolite an interesting molecular sieve and a high-cation exchange material [25].

Samples S6, S7 and S8 are characterized by peaks of hydroxysodalite and apatite, similarly as samples S9, S10, S12, S14, S15 and S16. Whereas samples S11 is defined by the presence of hydroxycancrinite. In samples S13, peaks typical for zeolite X, hydroxysodalite and apatite were identified.

Figure 3 shows SEM of sewage sludge ash. The structure of sewage sludge ash was non-porous.

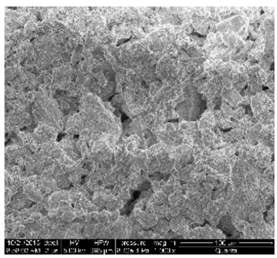

Fig. 3. SEM of sewage sludge ash, magn. 1000x

a) b) c) d)

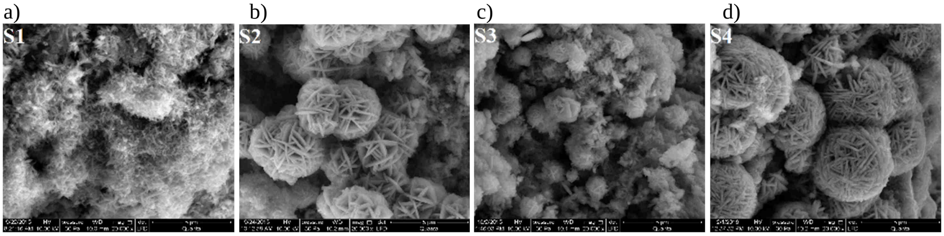

Fig. 4. SEM of sewage sludge ash after zeolitization by 6-hour crystallization and SSA:NaOH ratio of 1.0:1.4, magn. 20,000x

a) b) c) d)

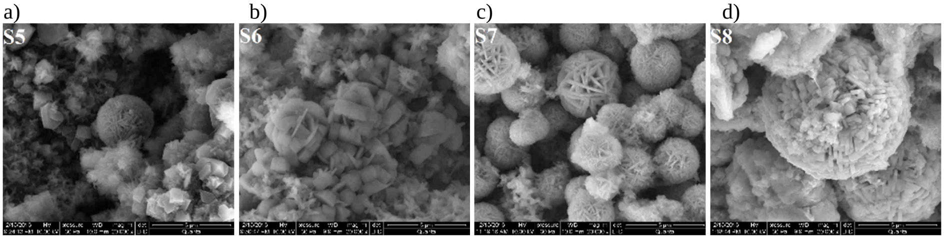

Fig. 5. SEM of sewage sludge ash after zeolitization by 72-hour crystallization and SSA:NaOH ratio of 1.0:1.4, magn. 20,000x

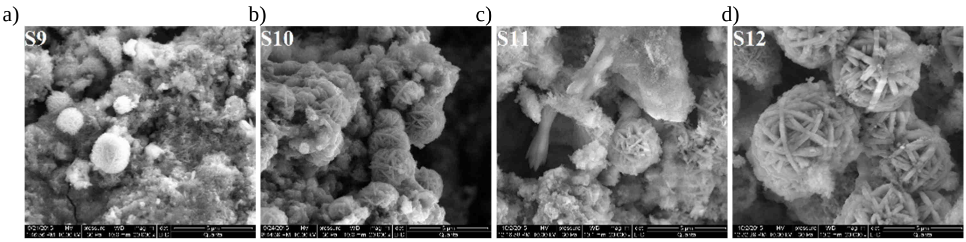

Fig. 6. SEM of sewage sludge ash after zeolitization by 6-hour crystallization and SSA:NaOH ratio of 1.0:1.8, magn. 20,000x

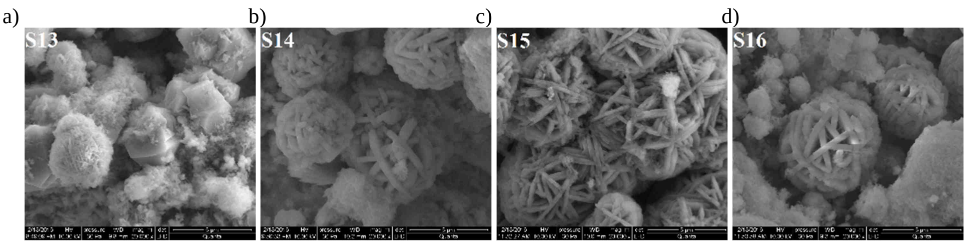

Fig. 7. SEM of sewage sludge ash after zeolitization by 72-hour crystallization and SSA:NaOH ratio of 1.0:1.8, magn. 20,000x

Figures 4-7 show the SEM images of the particles formed in this study. Figures 4b-d and Figures 5-7 present spherical shapes which correspond to hydoxysodalite. Figure 6c illustrates structures of long and sharp shapes characteristic for hydroxycancrinite. Figure 5a and Figure 7a demonstrate the octahedral morphology typical of zeolite X. Generally, the SEM images indicated that hydrothermal reactions during the process of zeolitization significantly changed the structure of samples.

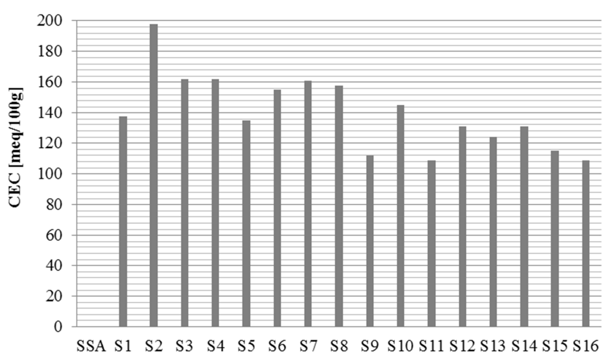

Fig. 8. CEC of sewage sludge ash and samples after zeolitization

The CEC results of sewage sludge ash and sewage sludge ash after zeolitization are presented in Figure 8. The CEC values of samples after zeolitization were within the range of 109.2-197.6 meq/100 g. Thus, the CEC values were higher in comparison to sewage sludge ash which was not subjected to modifications and lower than the values of commercial zeolites. The CEC values of commercial zeolites were within the range of 200-300 meq/100 g or even 900 meq/100 g [26, 27]. Moreover, the CEC values of tested samples did not depend on the parameters of the zeolitization process.

Conclusions

The study demonstrated the possibility of using sewage sludge ash for the synthesis of zeolites with a fusion method. Zeolite X was obtained for the SSA:NaOH ratio of 1:1.4 and 1:1.8. Other optimal parameters of the synthesis of zeolite X were identical for both samples, i.e. the activation and crystallization temperature of 60°C and the crystallization time of 72 hours.

The obtained zeolites can be used for the removal of contaminants from sewage.

The research proved that it is not easy to obtain only one type of zeolite from wastes. On the basis of the obtained test results, further work will be continued in order to improve the quality of the synthesized product.

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SYNTEZA ZEOLITÓW Z POPIOŁÓW Z OSADÓW ŚCIEKOWYCH

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Abstrakt: Skład chemiczny popiołów z osadów ściekowych jest podobny do składu chemicznego substratów stosowanych do syntezy zeolitów. W pracy przedstawiono wyniki zeolityzacji popiołów z osadów ściekowych metodą fuzji. Badania popiołów z osadów ściekowych przed oraz po procesie zeolityzacji obejmowały identyfikację składu fazowego (metoda XRD) oraz ocenę zmiany struktury ziaren (metoda SEM) i pojemności wymiany kationowej (metoda z wykorzystaniem octanu amonu). W popiołach z osadów ściekowych podanych zeolityzacji zidentyfikowano hydroksy sodalit, zeolit X oraz hydroksy kankrynit. Stwierdzono, że zeolityzacja spowodowała korzystny wzrost pojemności wymiany kationowej.

Słowa kluczowe: popiół z osadów ściekowych, zeolityzacja, hydroksy sodalit, hydroksy kankrynit, zeolit X, pojemność wymiany kationowej