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A simple thermogravimetric method for the evaluation of the degree of fly ash conversion into zeolite material

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Abstract The thermogravimetry was used for the evaluation of degree of conversion of fly ash into zeolite material alongside the CEC and XRD methods being currently proposed for this purpose. The present work proposes the calculation of the thermogravimetric fly ash-to-zeolite conversion factor, CF_{TGA}, based on the comparison of the mass loss of the commercial zeolite (standard) occurred during dehydration with that of the fly ash-derived zeolite. This mass loss is characteristic of a specific zeolite type, and the corresponding zeolite water content in the sample of zeolites indicates their degree of crystallinity and zeolite phase content. The use of the TGA method for the indirect determination of the fly ash-to-zeolite conversion factor would be preferable owing to its "speed" compared to other methods proposed for this purpose, as well as the capability to use a consistent procedure. Because of its short CF_{TGA} determination procedure, the thermogravimetric method can be used for the control and determination of the quality of fly ash-derived zeolite in an industrial plant.

Keywords TGA · Fly ash-derived zeolite · Thermogravimetric conversion factor CF

1 Introduction

Fly ash is a material which, in spite of offering a fairly large spectrum of utilization possibilities that have been recognized so far (the building industry, underground mining), still leaves room for searching new methods of application, that would enable its values, and particularly chemical composition, to be more fully exploited. This fact is confirmed by numerous publications dedicated to new possibilities of fly ash utilization, which include the synthesis of zeolites [1–6].

The main indicator of the quality of fly ash-derived zeolite is the degree of fly ash conversion into the zeolite material, called also with the term "zeolite purity" or degree of crystallinity (in the case where X-ray analysis is used to determine the degree of fly ash conversion into the zeolite material). The relevant literature does not provide a precise method for determining quantitatively the zeolite phase content in a sample, and the term "purer zeolite material" denotes the one with the highest degree of fly ash conversion into the zeolite material. The fly ash-to-zeolite conversion degree is only determined indirectly utilizing methods that are commonly used for the evaluation of the physicochemical properties of zeolites, such as: XRD (for identify the crystalline zeolite and its type), CEC (for determining the cation exchange capacity), IR (for distinguishing zeolite structures), and BET (for determining the specific area and volume of pores). The indirect determination of the conversion degree, referred to in this study as the conversion factor CF, consists in comparing the values obtained by these methods for fly ash-derived zeolites with the values obtained for commercial (pure) zeolites. Figure 1 summarizes the methods for the determination of the fly ash-to-zeolite conversion factor.

The majority of authors [7–13] determines the fly ash-to-zeolite conversion degree in an indirect manner by testing the cation exchange capacity, CEC. The fly ash-to-zeolite conversion factor is determined in this method by comparing the CEC value obtained for the fly ash zeolite

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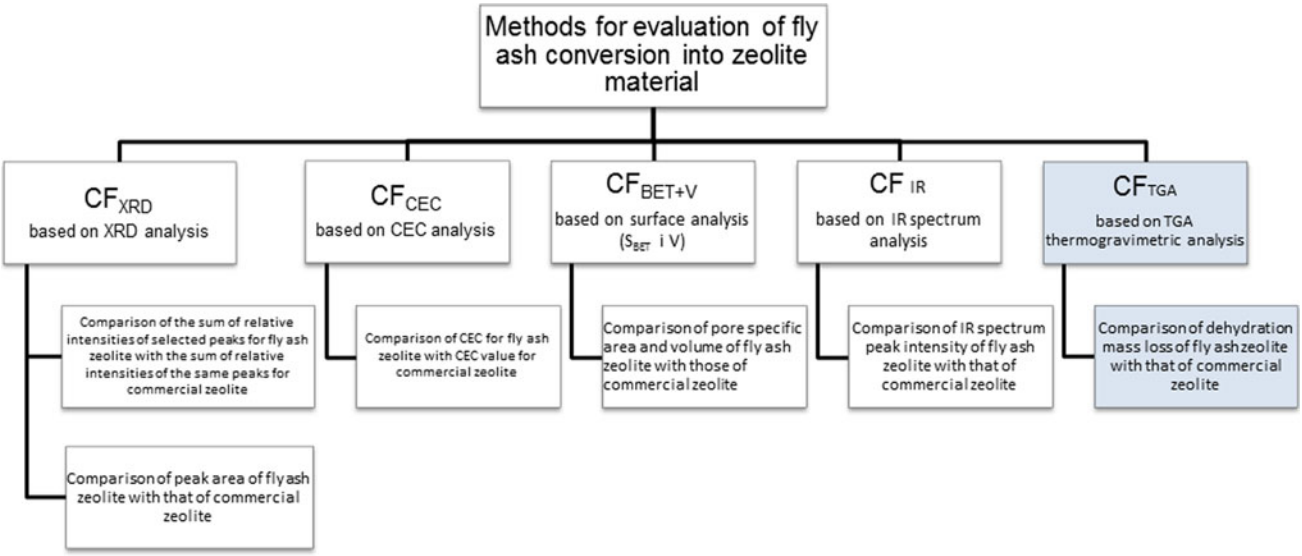


Fig. 1 Methods for the determination of the fly ash-to-zeolite conversion factor

material with the CEC value for the commercial zeolite of a purity of approx. 100 %. Unfortunately, CEC determination methodologies differ for different authors and are established for different ions, which is the source of numerous errors and makes the comparison of results difficult. Moreover, the CEC values depend on the temperature and, as shows by studies [14], also on the synthesis method and process parameters. Most often, the CEC is determined for the ions NH_4^+, Cd^{2+}, Pb^{2+}, Zn^{2+} and Ba^{2+} [6]. Another method being commonly used for the indirect determination of the fly ash-to-zeolite conversion degree is the quantitative XRD analysis. In the XRD method, the fly ash-to-zeolite conversion degree is evaluated via the analysis of the intensity of the main peak, the analysis of so called relative peak intensity and comparing the area of the peak for the fly ash zeolite with the area of the same peak for the commercial zeolite. According to the calculation methodology proposed by Rayalu et al. [15], the fly ash-to-zeolite conversion degree, as defined in the work as the X-ray conversion factor (CF_{XRD}), is expressed as the ratio of the sum of the relative intensities of 10 individual peaks characteristic of a given fly ash zeolite type (e.g. Na-A) to the sum of the relative intensities of 10 individual peaks characteristic of a standard (that is the commercial zeolite, e.g. Na-A). Rayalu et al. [15] have also proposed the use of IR spectroscopy for the determination of the fly ash-to-zeolite conversion degree by comparing the intensities of peaks at 560 cm^{-1} (asymmetric vibrations bending the Si(Al)-O bonding) and at 464 cm^{-1} (internal vibrations in tetrahedrons) of fly ash zeolite and commercial zeolite. This coefficient is defined in this work as the spectroscopic conversion factor (CF_{IR}). More recently, Gross et al. [16, 17] have proposed the determination of the conversion factor, which is referred to in this work as the surface conversion factor (CF_{BET+V}), by comparing the magnitudes of the surface area and volume of micropores of the fly ash zeolite with those of the commercial zeolite. The reported literature data show that there is no consistent methodology for the indirect determination of the fly ash-to-zeolite conversion factor, which make the comparison of results reported by different authors difficult. In addition, the presence of more than one zeolite phase hinders the use of the conversion factor determination methods described. Bearing in mind that each method is based on some simplifications, it would be necessary to rely on the results from several methods in order to obtain the complete information. It would be justifiable, therefore, to jointly use several methods to determine the CF and to check the possibility of using other research methods to this end. The thermogravimetric analysis (TGA), which is widely used for the evaluation of the degree of dehydration of zeolite materials and their thermal stability, has not been proposed to date for the indirect determination of the conversion factor. For the first time, such an attempt was made in the present work by developing the thermogravimetric conversion factor (CF_{TGA}).

The aim of this work was estimated the possibility of use of the thermogravimetric analysis (TGA), for the evaluation of the fly ash-to-zeolite conversion factor, CF_{TGA}.

2 Experimental

2.1 Synthesis

Zeolite synthesis reactions were carried out in a 5 L reaction vessel Hell, as presented in Fig. 2.The synthesis processes were run aimed at obtaining two zeolite phases,

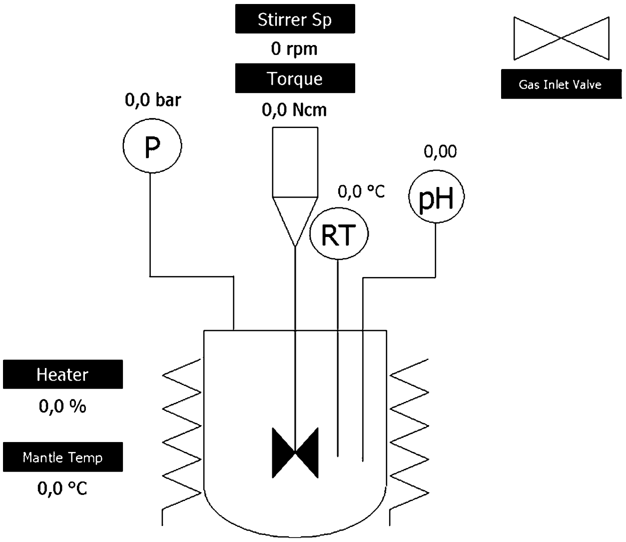


Fig. 2 Schematic diagram of the pressure reactor used for the syntheses of zeolite materials from fly ash

Na-A and Na-P1, differing in the content of the zeolite phase. Coal fly ash obtained from a utility power station in Poland (PC) was used for the synthesis. The fly ash was chemically analyzed and used to prepare the zeolite materials. The chemical composition of starting fly ash is given in Table 1. The main components of coal fly ash were SiO_2 and Al_2O_3. The SiO_2/Al_2O_3 ratio for fly ash used for zeolite synthesis was 2.43. The value of this ratio for zeolite synthesis is very important, as the formation of the particular zeolite species dependents on the Si/Al ratio in the starting material.

2.1.1 *Na-P1 zeolite*

For producing the Na-P1 zeolite material, the classic method was used, whereby fly ash (20 g) was mixed with a 2.0 mol/dm^3 sodium hydroxide solution (160 cm^3) and heated at 125 °C for 8, 12 and 24 h, respectively. Due to the fact that the Na-P1 zeolite samples obtained by this method had still a lot of impurities left from the fly ash, also high degree of purity Na-P1 zeolite was synthesized (following the 2-stage hydrothermal method based on the Si and Al fly ash extract, as proposed by [18]). To obtain the extract, a 2 mol/dm^3 NaOH solution was used, which was mixed with fly ash in a ratio of 2.5:1, heated for 6 h at a temperature of 90 °C and, finally, filtered. Thus obtained filtrate was heated at a temperature of 90 °C for 48 h to obtain a high degree of purity Na-P1 phase.

2.1.2 *Na-A zeolite*

For producing the Na-A zeolite, a synthesis based on the fly ash extract with an addition of sodium aluminate, Al_2O_3, was used, to obtain the Si/Al ratio in the initial gel appropriate for obtaining the Na-A zeolite phase. This ratio should be from 2 to 2.4. This method was employed with the aim of obtaining high degree of purity Na-A zeolite based on fly ash. In the first step (referred to as activation) an Si and Al filtrate was obtained from the fly ash by treating with an NaOH solution at 80–88 °C for 2 h. To optimize the process, NaOH solutions of varying concentrations, i.e. 1.5; 3.3; 5 and 6.5 mol/dm^3, were used. Using solutions varying in concentration made it possible to obtain filtrates of varying Si/Al ratio, because the dissolution degree of Si and Al depends on the solution concentration, increasing with its increase. Then, to each of the initial filtrates an additional aluminium source was added in the form of $NaAlO_2$ dissolved in the NaOH solution of the identical concentration as the one used for obtaining the initial filtrate. The addition of the same mount of $NaAlO_2$ to each of the obtained filtrates allowed initial gels for synthesis to be obtained in varying Si/Al ratio (2.0; 2.15; 2.4; 2.55, respectively, for using concentrations of 1.5; 3.3; 5 and 6.5 mol/dm^3). The addition of aluminium was necessary because of the low content of aluminium in the filtrates obtained from the fly ash. The second step, that is crystallization, was conducted using different synthesis durations (i.e. 3, 4, 5, and 6 h).

All the obtained samples were filtered, washed with distilled water in order to remove the remaining NaOH, and dried at 120 °C for 12 h. For comparison, the commercial (pure) Na-A and Na-P1 zeolite were also used for the tests.

2.2 Characterization

The formation of a zeolites was confirmed by powder X-ray diffraction. XRD patterns were recorded on a Bruker AXS D8 Advance diffractometer using CuKα radiation of wavelength 0.15405 nm. Diffraction data were recorded

Table 1 Chemical composition of fly ash (wt%)

Fly ash	Element as oxide										
	LOI*	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Mn_2O_3	P_2O_5	TiO_2	SiO_2/Al_2O_3
1	1.26	54.77	22.56	4.46	7.9	0.66	1.78	1.09	0.16	0.004	2	2.43

* *LOI* loss on ignition

between 6–60° 2Θ at an interval of 0.5° 2Θ. The X-ray method was also used for the calculation of the XRD factor of fly ash conversion to zeolite material (CF_{XRD}) by comparing the relative intensities of peaks characteristic of the Na-A and Na-P1 fly ash zeolites with the relative intensity of the same peaks for the commercial zeolites, following the procedure described in [15].

The cation exchange capacity (CEC) of zeolite materials was assessed based on the NH_4^+ ammonium ion exchange according to the US EPA SW-846 method described by Fan et al. [19]. The assay involves mixing of 4 g of zeolite sample with 33 cm^3 of sodium acetate solution (1 mol/dm^3) and shaking for 5 min, followed by decanting. The solid residue was shaken again with a fresh sodium acetate solution. The process was repeated 3 times, after which the solid residue was washed with 33 cm^3 of ethanol. Next, ammonium acetate solution (1 mol/dm^3) was added to exchange the absorbed sodium ions for ammonium ions. The obtained filtrate was diluted to 100 cm^3 with ammonium acetate solution (1 mol/dm^3) and the sodium concentration was determined by ion chromatography (using an 883 Basic IC plus chromatograph by Metrohm). The obtained CEC values were used for calculation of CF_{CEC} by comparing the CEC value obtained for the fly ash-derived zeolite with the CEC value for the commercial zeolite (standard). The effect of temperature on the zeolite samples was studied by a Mettler TGA/SDTA 851e thermobalance. The zeolite samples were heated up from room temperature to 500 °C at a rate of 20 °C min^{-1} in a flow (50 cm^3 min^{-1}) of nitrogen. The mass loss in the TG curve (25–500 °C) was chosen for the conversion factor calculations, as it is this stage that is connected with desorption of surface-adsorbed water, removal of water molecules from the channels/void system of the zeolite structure and dehydration of hydrated cations positioned in the zeolite framework.

All measurements were blank-curve corrected. For temperature calibration, standard substances of known phase change temperatures were used.

3 Results and discussion

3.1 Characterization of fly ash-derived zeolite

The diffraction patterns for the Na-P1 products obtained by two methods are shown in Fig. 3.

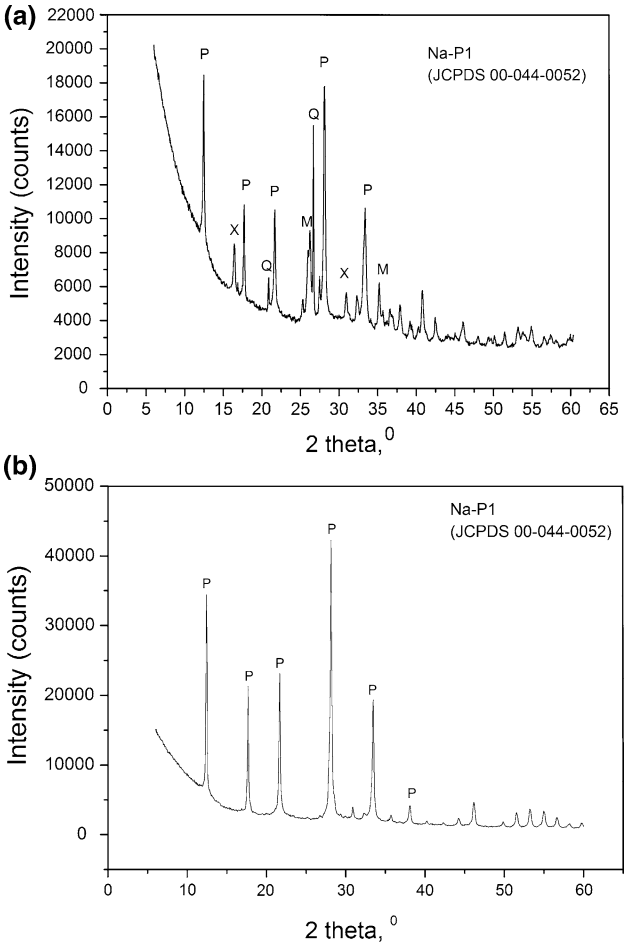
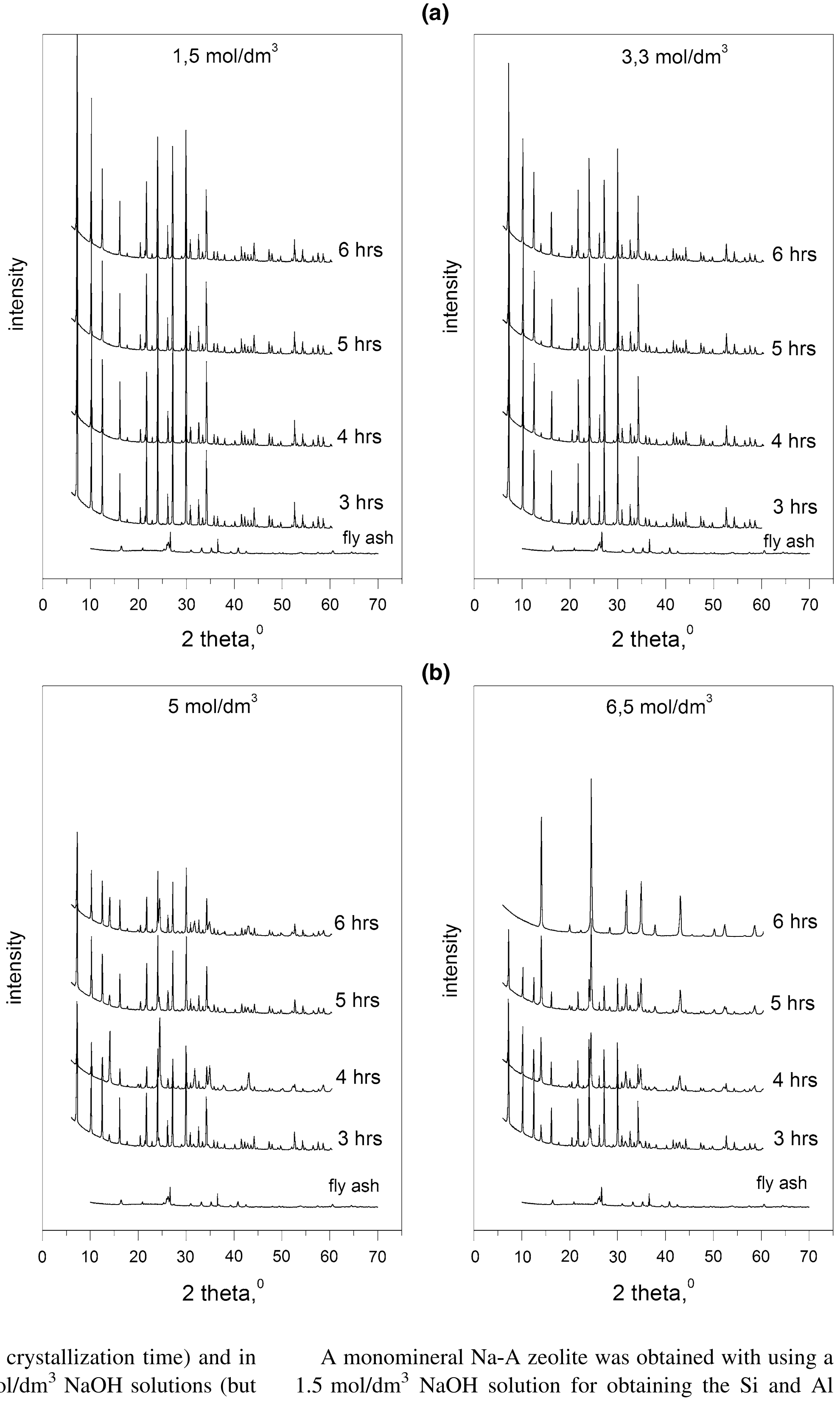


Fig. 3 XRD of the Na-P1 zeolite phases obtained by fly ash modification **a** as obtained by the hydrothermal method; **b** as obtained by the 2-stage method: *Q* quartz, *M* mullite, *P* Na-P1 zeolite, *X* F-FAU zeolite

In the case of using 2 mol/dm^3 NaOH solution (Fig. 3a), with the increase in synthesis duration, the intensity of the $I_{Na\text{-}P1(301)}$ peak increases, which is indicative of an increased Na-P1 zeolite content of the sample. At the same time, the intensity of the quartz characteristic peak, I_Q, increases, which confirms the solution of the quartz and its inclusion in the reaction, which increase with the synthesis time. In Fig. 3a we can notice the unchanging intensity of the mullite characteristic peak, I_M, which confirms the fact that regardless the synthesis duration the mullite does not dissolve in the alkaline medium and does not enter into reaction. As a result of the performed two-stage hydrothermal synthesis based on the fly ash Si and Al extract (Fig. 3b), a Na-P1 zeolite with a high degree of purity was obtained, which could be inferred from the XRD (no peaks characteristic of fly ash).

Figure 4 shows XRD diffraction patterns for the Na-A zeolite products obtained as a result of the syntheses carried out. As can be noticed from Fig. 4, in all of the synthesis conditions used, the Na-A zeolite phase was obtained in the samples, except for the sample activated with the 6.5 mol/dm^3 NaOH solution and then subjected to 6 h' crystallization. The presence of (hydroxyl) sodalite was found in that sample. This zeolite accompanied the Na-A phase in the case of making activation with the 6.5 mol/dm^3

Fig. 4 XRD of the zeolite materials obtained by the method based on the fly ash extract with the addition of sodium aluminate, $NaAlO_2$, while making fly ash activation with NaOH solution in a concentration of 1.5; 3.3 (**a**) and 5; 6.5 mol/dm^3 (**b**) (at 80 °C for 2 h) and conducting crystallization at 100–105 °C for 3, 4, 5 and 6 h, respectively



NaOH solution (regardless the crystallization time) and in the case of using 3.3 and 5 mol/dm^3 NaOH solutions (but only with 3 h' crystallization time, and that were only traces). In other cases, a high degree of purity Na-A zeolite was obtained.

A monomineral Na-A zeolite was obtained with using a 1.5 mol/dm^3 NaOH solution for obtaining the Si and Al filtrate, regardless the crystallization time, which indicates that this is the most favourable NaOH concentration for obtaining the filtrate suitable for recovering the high degree

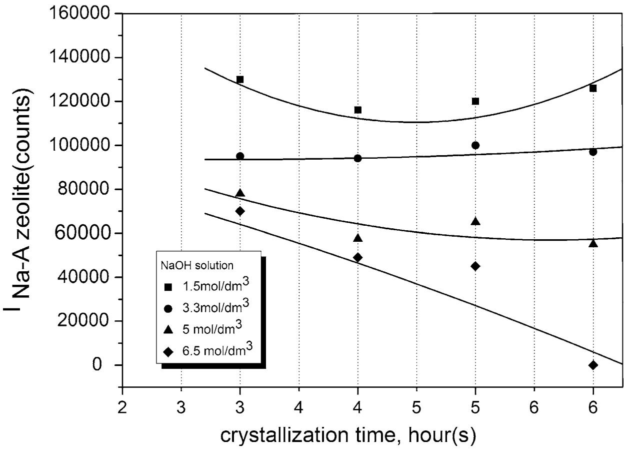


Fig. 5 Dependence of the (200) diffraction peak intensity on the crystallization time at different NaOH concentrations *square* experimental data; *solid line* simulated data

of purity Na-A zeolite from the fly ash by this method (the Si/Al after adding $NaAlO_2 = 2.0$).

The synthesis result was represented by the intensity I_A, of the most intense diffraction peak for fly ash-derived Na-A zeolite (Fig. 4) corresponding to the (200) Miller's indices ($2\theta = 7.178$). Figure 5 represents the dependence of the (200) diffraction peak intensity, I_A, of the Na-A zeolite on the crystallization time at different NaOH concentrations used for obtaining the Si and Al extract from the fly ash. As follows from Fig. 5, with increasing crystallization time, the (200) diffraction peak intensity, I_A, of the Na-A zeolite slightly increases in the case, where the 1.5 and 3.3 mol/dm^3 NaOH solutions were used for fly ash activation, and decreases with increasing crystallization time, when 5 and 6.5 mol/dm^3 NaOH solutions were used for fly ash activation. The highest (200) diffraction peak intensities, I_A, of the Na-A zeolite are observed in the case of using the 1.5 mol/dm^3 NaOH solution for activation. Thus, when NaOH solutions of higher concentrations are used, shorter crystallization times are definitely more advantageous, as the Na-A phase content of the sample decreases with increasing crystallization time. In the case of using lower concentrations of NaOH solution, the crystallization time plays a less important role, and a material of a substantial Na-A phase content can be obtained already after 3 h of crystallization. The degree of fly ash conversion to Na-P1 and Na-A zeolite materials was evaluated by calculating the thermogravimetric factor of conversion (CF_{TGA}) of fly ash to the zeolite material, as proposed in the study.

3.2 Thermogravimetric fly ash-to-zeolite conversion factor-CF_{TGA}

Tests of the dehydration of fly ash zeolites carried out by the thermogravimetric method [20] have suggested a possibility of using this method for the evaluation of degree of conversion of fly ash into zeolite material alongside the CEC, XRD, BET and IR methods being currently proposed for this purpose. The present work proposes the calculation of the thermogravimetric fly ash-to-zeolite conversion factor, CF_{TGA}, based on the comparison of the mass loss of the commercial (pure) zeolite occurred during dehydration with that of the fly ash-derived zeolite. This mass loss is characteristic of a specific zeolite type, and the corresponding zeolite water content of the zeolite sample indicates their degree of crystallinity and zeolite phase content [21]. The basis for the determination of the conversion factor CF_{TGA} are the TG curves of mass loss during heating of the commercial zeolite (standard) and the fly ash-derived zeolite. From the obtained values, the percentage fly ash-to-zeolite conversion factor, CF_{TGA}, can be obtained, which is the ratio of the mass loss of the fly ash zeolite (due to its dehydration) to the mass loss (due to dehydration) of the commercial zeolite (standard) synthesized classically from chemically pure components, according for formula 1.

$$CF_{TGA}[\%] = \frac{\text{The mass loss of the fly ash zeolite (due to its dehydration)}}{\text{The mass loss of the commercial zeolite} - \text{standard (due to its dehydration)}} \times 100 \quad (1)$$

Figure 6 shows TG curves for Na-P1 zeolites obtained from fly ash by hydrothermal synthesis (using 2 mol/dm^3 NaOH solutions, 125 °C, and a synthesis duration of 8, 12 and 24 h), as well as for an Na-P1 zeolite produced from an Si fly ash extract by a two-stage method. Based on the values red out from the TG mass loss curves and using formula (1), CF_{TGA} thermogravimetric conversion factors were calculated, which amounted to 55, 76.5 and 62 %, respectively, for the Na-P1 zeolites obtained after 8, 12 and 24 h of crystallization, and 91 % for the Na-P1 zeolite produced from the fly ash extract by the two-stage method. The obtained values show that in the case of the hydrothermal conversion of fly ash into the zeolite Na-P1 the most favourable synthesis duration was 12 h (using a

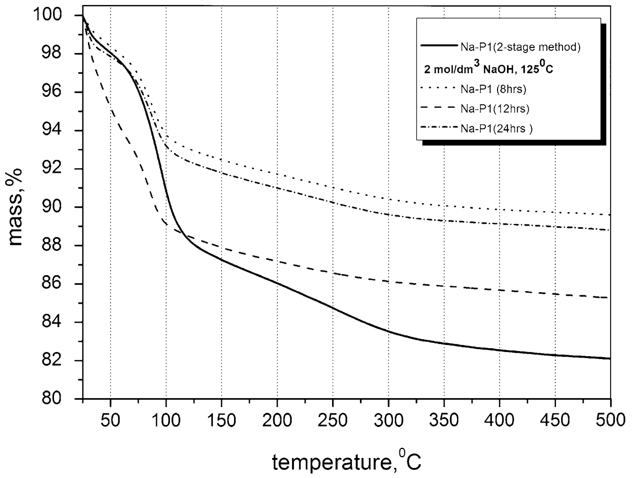


Fig. 6 Thermogravimetric (*TG*) *curves* of Na-P1 zeolite obtained from fly ash by hydrothermal activation (using a 2 mol/dm^3 NaOH solution, 125 °C, and a synthesis duration of 8, 12 and 24 h) and from an Si fly ash extract by a two-stage method, respectively (heating rate: 20 °C min^{-1}; nitrogen flow: 50 cm^3 min^{-1})

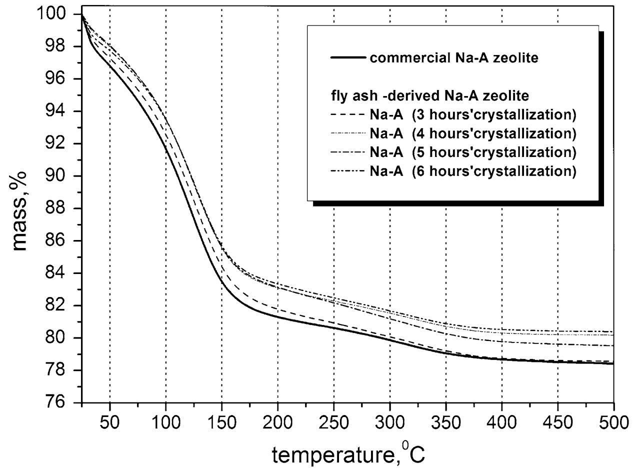


Fig. 7 Thermogravimetric (*TG*) *curves* of commercial Na-A zeolite and Na-A zeolites produced from fly ash as a result of hydrothermal reaction based on the fly ash extract using a 3.3 mol/dm^3 NaOH solution and after 3, 4, 5 and 6 h' crystallization (heating rate: 20 °C min^{-1}; nitrogen flow: 50 cm^3 min^{-1})

2 mol/dm^3 NaOH solution, at 125 °C). The lower values of the fly ash-to-zeolite conversion factor achieved for the Na-P1 zeolites produced by the direct hydrothermal conversion method indicate that the zeolites obtained by this method contain considerable amounts of impurities left from the fly ash. Calculations of the $\mathrm{CF_{TGA}}$ thermogravimetric conversion factor were also carried out for Na-A zeolite obtained by the direct hydrothermal activation method. Figure 7 represents TG curves for the commercial Na-A zeolite (standard) and for Na-A zeolites obtained from fly ash as a result of hydrothermal activation based on the fly ash extract with the use of a 3.3 mol/dm^3 NaOH solution and after crystallization for 3, 4, 5 and 6 h. Based on the values red out from the TG curves (Fig. 7) and using formula (1), $\mathrm{CF_{TGA}}$ thermogravimetric conversion factors were calculated, which amounted to 99, 92, 94.1 and 90 % for Na-A zeolites obtained after 3, 4, 5 and 6 h of crystallization, respectively. The high degrees of fly ash conversion into the Na-A zeolite material confirm that zeolites of a high purity level can be produced by the fly ash extract synthesis method. TG curves-based conversion factors were also calculated for Na-A zeolites obtained using 1.5; 5 and 6.5 mol/dm^3 NaOH solutions and 3, 4, 5 and 6 h' crystallization. For the Na-A zeolites produced using the 1.5 mol/dm^3 solution, the $\mathrm{CF_{TGA}}$ conversion factor ranged from 92 to 96.8 %; for the Na-A zeolites produced using the 5 mol/dm^3 solution, from 80 to 97.7 %; and for the Na-A zeolites produced using the 6.5 mol/dm^3 solution, from 65 to 88.2 %. A summary of $\mathrm{CF_{TGA}}$ thermogravimetric conversion factor values for Na-A zeolites produced by fly ash extract hydrothermal activation under different synthesis conditions, including time and NaOH concentration, is provided in Fig. 8. The obtained results indicate a lower fly ash-to-zeolite conversion degree in the fly ash extract synthesis method in the case of using NaOH solutions of a higher concentration and longer crystallization times. The obtained results for the thermogravimetric conversion factor ($\mathrm{CF_{TGA}}$) for the zeolites Na-P1 and Na-A were compared with the values of the X-ray conversion factor ($\mathrm{CF_{XRD}}$) and the CEC conversion factor ($\mathrm{CF_{CEC}}$) of the fly ash-derived zeolite materials. The fly ash-to-zeolite conversion degree results obtained for Na-P1 zeolites and selected Na-A zeolite materials are given in Table 2. As can be seen from the data in Table 2, the results obtained by different methods differ, which indicates how important it is to specify the procedure and methodology of calculating the fly ash-to-zeolite conversion degree when reporting the results of syntheses.

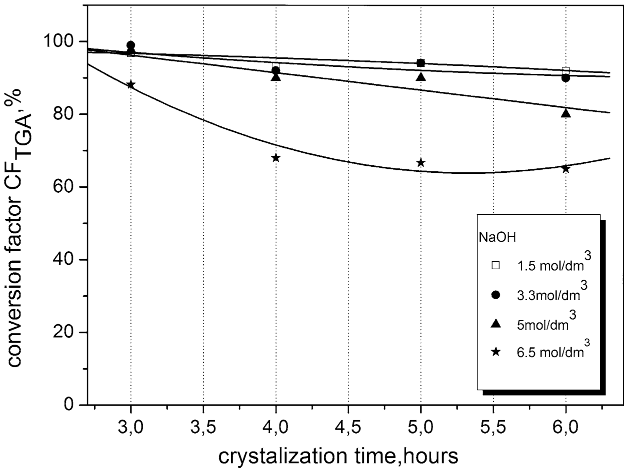


Fig. 8 $\mathrm{CF_{TGA}}$ thermogravimetric conversion factors for fly ash-derived Na-A zeolite obtained from the fly ash extract by the hydrothermal activation method

Table 2 The fly ash-to-zeolite conversion factor (%) as determined by the CEC, XRD and TGA methods for selected fly ash-derived zeolite

	Conversion factor (CF)		
	CF_{CEC} (%)	CF_{XRD} (%)	CF_{TGA} (%)
Commercial zeolite			
Na-A	100	100	100
Na-P1	100	100	100
Fly ash-derived zeolite			
Na-P1	92.0	94.0	91.0
Na-P1 (2 mol/dm^3, 8 h)	63.7	52.0	55.0
Na-P1 (2 mol/dm^3, 12 h)	77.4	72.0	76.5
Na-P1 (2 mol/dm^3, 24 h)	74.1	52.0	62.0
Na-A (3.3 mol/dm^3, 3 h)	98.0	92.7	99.0
Na-A (3.3 mol/dm^3, 4 h)	98.5	92.0	92.0
Na-A (3.3 mol/dm^3, 5 h)	94.9	94.0	94.1
Na-A (3.3 mol/dm^3, 6 h)	93.5	93.5	90.0

4 Conclusions

The use of the TGA method for the indirect determination of the fly ash-to-zeolite conversion factor would be preferable owing to its “speed” compared to other methods proposed for this purpose, as well as the capability to use a consistent procedure. Because of its short CF_{TGA} determination procedure, the thermogravimetric method can be used for the control and determination of the quality of fly ash zeolite products in an industrial plant.

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