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THERMAL TRANSFORMATION OF COMBUSTION WASTES FROM COAL-FIRED BOILERS

TERMICZNE PRZEKSZTAŁCANIE ODPADÓW POWSTAŁYCH ZE SPALANIA WĘGLA W KOTŁACH PYŁOWYCH

The results of the lab-scale investigations concerning vitrification process of the fly ashes formed during the coal combustion in the boiler are presented in the paper. The fly ashes used at the laboratory studies were collected from thermal power plants fired by lignite and bituminous coal, respectively. The tests were carried out in the fixed bed reactor applying electrical method of the vitrification. The properties of the ash glasses obtained after the vitrification by means of their leachability and durability were examined and discussed. The minerals crystallisation in the vitrification glass was investigated using the XRD method. The effect of the heat treatment on the glass and glass-ceramic durability performing the hardness measurement was examined, as well. The results revealed high effectiveness of the vitrification method. The glasses from coal fly ashes had amorphous texture and were characterized by high physical durability as well as very low leachability caused by successful immobilization of the heavy metals into the glass structure.
Keywords: fly ash, glass-ceramic, heavy metals, vitrification

W pracy przedstawiono wyniki badań laboratoryjnych nad możliwością wykorzystania procesu witryfikacji do zeszklenia popiołów lotnych pochodzących ze spalania węgla w kotłach pyłowych. Do badań użyto popioły lotne z polskich elektrowni pochodzące ze spalania węgli kamiennych i brunatnych. Badania doświadczalne przeprowadzono w reaktorze typu złoże stałe stosując elektryczną metodę witryfikacji. Przedstawiono i omówiono wyniki badań wymywalności i twardości uzyskanych szkieł w procesie witryfikacji. Zbadano także strukturę krystaliczną otrzymanych witryfikatów metodą XRD. Wykonano również badania wpływu dodatkowego wygrzewania witryfikatów na poprawę ich własności mechanicznych. Otrzymane wyniki pokazały, że witryfikacja jest skuteczną metodą umożliwiającą modyfikację właściwości lotnych popiołów. Wykazano, że powstałe z popiołów lotnych szkła posiadają amorficzną strukturę i charakteryzują się wysoką twardością oraz niską wymywalnością metali ciężkich, które zostały wbudowane w sieć krystaliczną szkła.

1. Introduction

In polish power engineering more than 96% of the electric energy is produced burning coal. As a result, in Poland ca. 12 °10^6 Mg/year of fly ashes are generated. In the world the fly ash production exceeds 10^9 Mg/year. The combustion wastes from PF boilers consist of fly ash (80-90%) and the slag (10-15%) [1]. Fly ash is a waste from combustion process of the pulverized solid fuels, such as: coal, biomass, coke, peat etc. which leaves the furnace of PF/CFB boiler together with a flue gas. Its form is a very fine mineral dust in colour from light to dark grey or light-brown and consists mainly of silicon, aluminium and iron compounds.

The constituents of the ash are primarily oxides of Si (SiO_2), Al (Al_2O_3), Fe (Fe_2O_3), Ca (CaO), Mg (MgO), Na (Na_2O), K (K_2O), and Ti (TiO_2).

The elemental and phase composition of ashes depends on the mineral matter of coal and the burning technology. In the ash four main groups of the components can be distinguished [2]:

- matrix components (SiO_2, Al_2O_3, Fe_2O_3, CaO),
- basic components (MgO, SO_3, Na_2O, K_2O),
- by-product components (TiO_2, P_2O_5, MnO and others),
- unburnt carbon.

In the matrix the most important are aluminiumsilicates compounds, which cause that the ashes are faintly water-soluble. The rates of the matrix components share determine the most important properties of fly ashes and their further classification.

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Depending on the application various fly ashes classifications were introduced. Taking into account the major components, the fly ashes in Poland are divided into three groups shown in Table 1.

TABLE 1

Fly ashes classification (BN-79/6722-09)

Kind of ash	Symbol	Content, wt %			
		SiO_2	Al_2O_3	CaO	SO_3
Silicate	**k**	> 40	< 30	⩽ 10	< 4
Aluminium	**g**	> 40	⩾ 30	⩽ 10	< 3
Calcium	**w**	> 30	< 30	> 10	⩾ 3

In the literature can be found also another fly ashes classification. For example, in the cement industry the fly ashes are classified as shown in Table 2.

TABLE 2

Fly ashes classification in cement industry [3, 4]

Ash class	Symbol	Content, wt %			
		SiO_2	Al_2O_3	Fe_2O_3	CaO
Low calcareous	**F**	> 70			< 5
High calcareous	**C**	> 50			> 20

The management of these combustion wastes is a responsibility of the heat and power producers. Unfortunately, landfill and storage of fly ashes is very expensive and causes several environmental problems [1, 3, 5]:

- pollution of the soil with organic compounds (dioxins and furans),
- leaching of heavy metals,
- secondary dust production.

The most serious problem of the fly ash storage is leaching of heavy metals from deposited fly ash into the soil leading to the contamination of groundwater with toxic heavy metals (B, Cu, Sr, Ni, Cr, Cd, Zn, Pb, Se, Hg, As, etc) [3, 6]. The presence of the heavy metals in the fly ash is normal, because they are present in coal and after the coal combustion the non-volatile heavy metals remains and concentrates in the ash [7]. Although, the concentration of heavy metals in the fly ash from coal-fired boilers is not high (only a few hundred ppm), their impact on the pollution of the environment is relevant. Moreover, the migration of heavy metals into the soil is governed by the ion-exchange mechanism, which depends on several factors, such as: pH and the presence of alkali and alkali-earth metals in the soil. Therefore, the hazard of the contamination of ground waters with toxic heavy metals due to landfill of fly ashes should be considered carefully.

In this connection, the companies are looking for their practical applications to reduce the management expenditures. One of the possibilities is the use of fly ashes to remove the metallic impurities from sewages. Fly ashes consisting mainly of aluminium silicates are very interesting alternative to heavy metals adsorbents being widely applied in the sewage/waste water treatment technologies.

The purpose of the research carried out was to investigate the effectiveness of the immobilisation of heavy metals in fly ash by the vitrification method, and next, to examine the possibility of improving of the mechanical properties of the vitrification product by heat treatment.

2. Immobilisation of heavy metals in fly ash

The required effectiveness of stabilisation of wastes in an immobilising material depends on the hazard caused by the waste. For example, radioactive wastes should be long-term immobilised (100 years). Therefore, different methods of heavy metal immobilisation were developed:

– stabilisation in concrete,
– immobilisation using alumina and thermal treatment,
– zeolitization of fly ash,
– pelletization and thermal treatment,
– vitrification.

Amongst the methods of waste stabilisation, vitrification is the most effective in the prevention of heavy metals leaching from fly ash, due to the effective immobilisation of metal atoms in the aluminosilicate matrix of the vitrification product. However, the method is the most expensive one, therefore for the time being it is applied only in case of very dangerous wastes, like a stabilisation of radioactive wastes and polluted soil.

3. Vitrification

Vitrification is a high-temperature process (Fig. 1), in which inorganic substances undergo melting and dissolution in the melted pulp, and organic substances undergo pyrolysis and burning. Then, the melted pulp is fast cooled and transformed into a chemically stable glaze (glass).

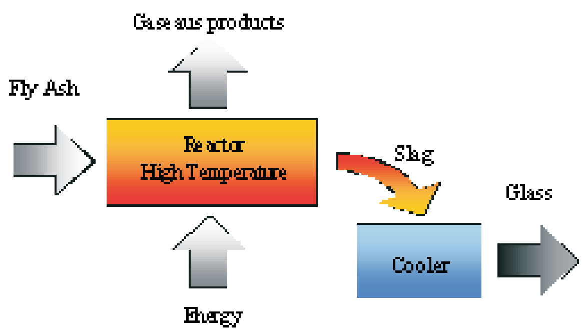

Fig. 1. Schematics of the vitrification process

A significant advantage of the vitrification is a permanent binding of heavy metals and radioactive elements in the silicates structure created in the glaze process. The final product (glaze) can be safely and commercially used or stored. Formation of the glaze involves both considerable decrease of the volume of the utilized waste and almost complete thermal destruction of the organic matter thanks to the high temperature of the process. It is important that only small quantities of secondary wastes are formed.

Vitrification has found applications in waste incineration because of several positive effects, like:

- volume and mass reduction,
- incineration of organic matter,
- immobilisation of heavy metals,
- chemical durability of glass,
- possibility of utilization of the vitrification products.

The process can be guided in various conditions and devices as well as concern different groups of substances [8-12]. There are several methods of vitrification depending on the form of energy supplied to the high temperature reactor. In most applications electrical methods are in use. Joule, plasma, microwave, induction and electric arc heating are the electric processes currently being applied to vitrification [13]. Because of very high temperatures is required, plasma methods of vitrification are considered as the most effective [14].

4. Lab-scale experimental investigations

The electrical method of vitrification with the use of Joule heat was used during the experimental investigations. The tests contained following issues and analysis:

- examination of the leachability of fly ash and the products of vitrification for four metals (cadmium, chromium, lead and zinc) according to the Polish standards [15],
- determination of the crystalline structure of fly ash and the vitrification products applying X-ray diffractometry (XRD),
- microstructural characterisation of the vitrification glass and glass-ceramic after heat treatment using standard metallographic techniques and scanning electron microscopy (SEM),
- measurements of the mechanical properties (micro hardness) of the vitrification products applying Vickers method.

Fly ashes used during the tests

The fly ashes used in the investigations were collected from the dedusting systems of the pulverized lignite and hard coal fired boilers (PC I and PC II) and the lignite fired fluidised bed boiler (CFB III) from two power plants in Poland (Table 3). The PC boilers were operating without dry desulphurisation systems. Flue gas from the CFB boiler were desulphurized by adding limestone into the combustion furnace of the boiler.

TABLE 3

Chemical composition of fly ashes

Compound	Content, % wt.		
	Power plants		
	EC Czechnica ash PC I	EL Turów ash PC II	EL Turów ash CFB III
SiO_2	77.8	69.6	40.11
Al_2O_3	6.71	14.6	25.97
Fe_2O_3	4.03	3.96	5.72
CaO	0.64	0.31	16.63
MgO	1.68	1.16	0.56
Na_2O	0.35	2.54	0.61
K_2O	0.63	0.68	2.66
SO_3	0.62	0.38	3.26
the rest	7.54	6.77	4.48
LOI	4.30	4.50	3.30

Fly ash PC (I and II) is a class F ash (the silica-alumina type). The Ca-rich fly ash CFB III is a class C ash and can be classified as a sulfo-calcic type. The basic difference between ashes of classes C and F is the CaO content [3, 16].

It could be expected that there would be differences between the phase composition of the CFB and PC ashes collected from Power Plants, due to the lower temperature in the fluidised bed furnace (800-900 °C) compared with that in the tangentially firing PC furnace (1200-1250 °C). The XRD graphs (presenting main crystalline components and amorphous or glassy material in the ashes [17]) obtained for ashes produced by two different combustion technologies are shown in Figure 2.

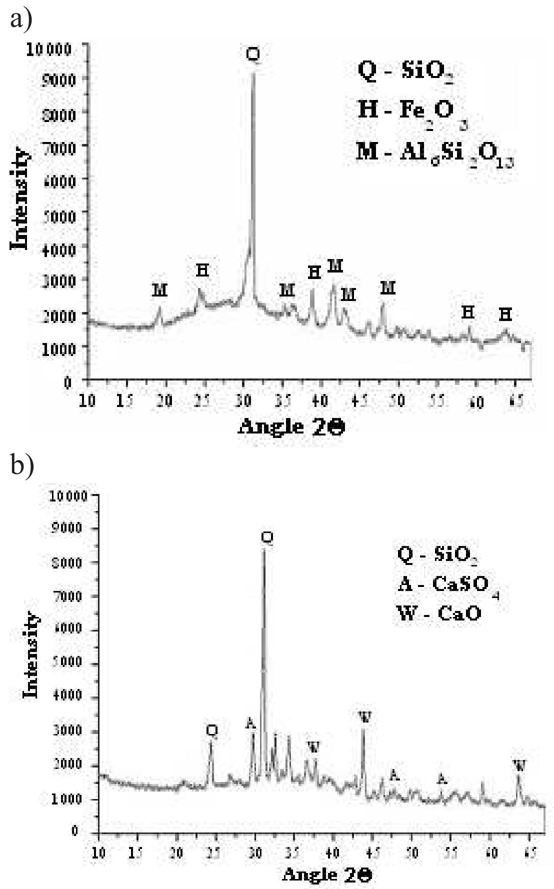

Fig. 2. XRD spectra for fly ashes: a) PC (II), b) CFB (III)

As could be expected, in the fly ashes PC (II) and CFB (III) quartz was the dominant crystalline component. For PC II, lines due to mullite ($Al_6Si_2O_{13}$) and hematite (Fe_2O_3) were also identified. Ash CFB III contained anhydrite ($CaSO_4$) as well as CaO. Both ashes also contained amorphous material that may be an unburned carbon. In case of ash PC II, it could be a glassy material.

5. Effect of vitrification and heat treatment on fly ash structure

The properties of the vitrification products may be improved applying thermal stabilisation of the material. In that aim the samples of the vitrification products of lignite and hard coal fly ash were put into the oven and held for 24 h at the temperature 800 °C and cooled afterwards slowly with a rate of 100 °C/h.

The effect of vitrification on the structure of mineral matter in the fly ash was investigated using the XRD analysis (Fig. 3). Common minerals having crystalline structure form about 10-30% of fly ash. The dominant minerals in the fly ash were: quartz, hematite and mullite. During the fly ash vitrification the crystalline structure of minerals was destroyed and the product obtained a perfectly amorphous structure. The only one peak in the diffractogram of the glass (Fig. 3) corresponds to the presence of metallic iron.

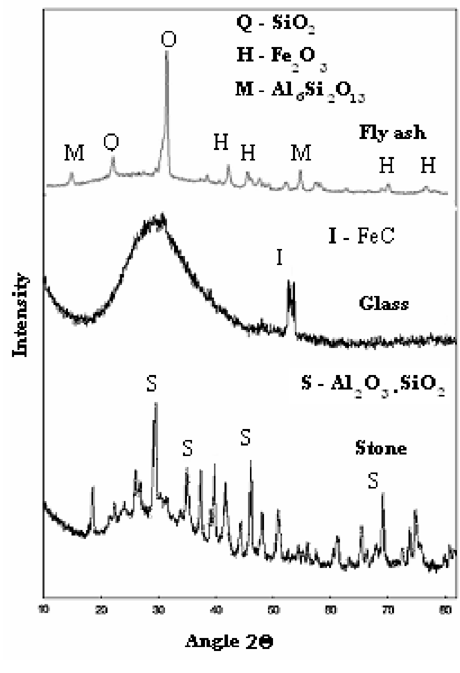

Fig. 3. Phase composition changes of the vitrification product (EC Czechnica PC I) [21]

After the thermal treatment the origins of crystallisation of glass-ceramic were observed. The XRD analysis revealed that the crystallised mineral (Fig. 3) was silimanite ($Al_2O_3.SiO_2$).

The more detailed SEM analysis of the vitrification product was also performed, the results are shown in Figures 4 and 5 [17].

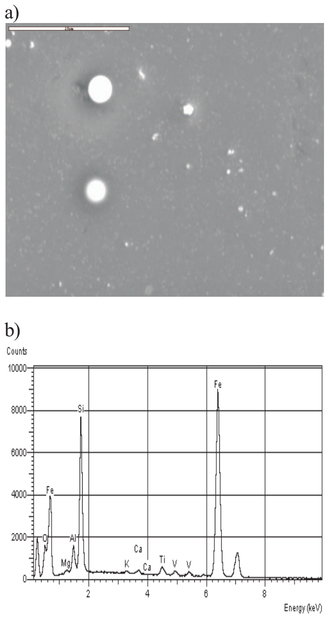

Fig. 4. Elementary analysis and SEM of the vitrified product PC I (EC Czechnica)

SEM photograph in connection with elementary analysis (Fig. 4) indicated the presence of fine iron elements in glass [17].

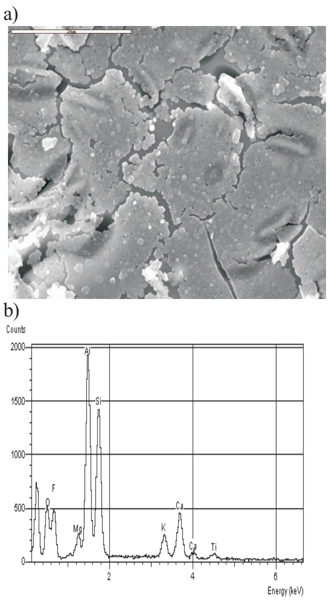

Fig. 5. Elementary analysis and SEM of the vitrified product PC I (EC Czechnica) after thermal treatment

It can be observed (Fig. 5) that the thermal stabilisation of the vitrification product results in its recrystallisation. The advantage of such transformation is a substantial decrease or elimination of the leachability of the heavy metals from the glaze.

6. Mechanical properties of the vitrification products

The waste materials can be used as building materials if they are environmental friendly and their mechanical properties meet the standards. Although the vitrification products are assigned for such applications (roads and buildings construction) to improve more their mechanical durability they are additionally thermally modified (as described previously).

The influence of the thermal stabilisation (recrystallisation) of the glaze on the mechanical properties was examined by measuring the micro hardness of modified samples of the material with the Vickers method [18]. Then, the results were compared with the hardness of glaze prior thermal processing (Fig. 6).

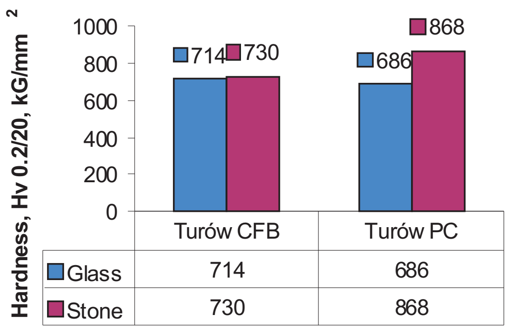

Fig. 6. Comparison of hardness of glass and stone (glass-ceramic) [21]

The improvement of vitrification product properties was observed for both types of the fly ash (from PC and CFB boilers). However, the significant increase of the stone (glaze after thermal treatment) hardness was identified for a final product PC II from power plant EL Turów (boiler OP-650b fired by lignite). The measured hardness of the stone in Mohs scale came to 6, which is equal to the hardness of magnetite [19].

7. Leaching tests

In the frame of the subject discussed in that paper, the leaching test relates to the susceptibility of the fly ash or glass to the extraction of the heavy metals under the influence of water impact. While the fly ashes are stored or applied as a building material, the leaching resistance is one of the crucial parameters from environmental point of view, because the release of the heavy metals to the ground leads to the serious water contamination and dangerous effluents formation [20, 21]. Because the vitrification process of fly ashes should limit the leaching process remarkably, the tests were performed to confirm such propensity.

The procedure applied during the leaching tests was in accordance with Polish standards (PN-Z-15009) and Ordinance of Ministers Council [22]. Then the chemical analysis of the waste water filtrate samples in view of heavy metals content was performed. The pH of the water and its conductivity were examined as well. The results are shown in Table 4.

TABLE 4

Leaching tests of heavy metals from fly ashes and vitrified products [17]

Element	Content in water, mg/dm^3			
	Ash PC II EL Turów		Ash PC I EC Czechnica	
	Fly Ash	Glass	Fly Ash	Glass
Cadmium	0.0019	0.0006	0.004	0.0006
Zinc	0.035	0.010	0.020	0.018
Chromium	0.025	0.006	0.15	0.0037
Lead	0.008	0.005	0.013	0.006
pH	9.51	6.74	11.96	6.82
Conductivity mS/cm	1.300	0.021	5.320	0.021

The received results of the analysis confirmed that the vitrification of fly ashes considerably reduces the leaching of heavy metals. For all investigated heavy metals the reduction of leaching was clearly observed. The largest differences in fly ash and glass effluents were measured for cadmium and chromium, while considerably smaller for zinc and lead. It should be marked that a pH underwent also essential changes, from basic one (exit fly ash) to the neutral one (vitrified fly ash). The conductivity has changed also remarkably after the transformation into the glass structure.

8. Conclusions

Vitrification process is an effective method of the neutralization of fly ashes and prevention against the leaching of heavy metals to the ground water. Due to the immobilisation of metal atoms into an aluminosilicate matrix the product of vitrification is environmentally safe. Moreover, the glaze received after the vitrification process is characterized by very good mechanical durability enabling its use as a building material. If it is required, additional improvement of mechanical durability of the vitrification product can be obtained applying the thermal treatment process.

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