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MACIEJ MAZURKIEWICZ*, EWELINA TKACZEWSKA**, RADOSŁAW POMYKAŁA**,
ALICJA ULIASZ-BOCHEŃCZYK***

Preliminary determination of the suitability of slags resulting from coal gasification as a pozzolanic raw material

Introduction

Poland is a country where power production is based on the combustion of coal and lignite. Traditional coal combustion technology is connected with high emissions of pollutants into the atmosphere, which is controlled by environmental regulations and the purchase of CO_2 allowances. For this reason, new technologies are implemented allowing for a reduction in the emission of (among other pollutants) CO_2, NO_x, and SO_2. The energy sector might introduce gas-steam units with integrated fuel gasification capabilities. This technology results in high energy efficiency and low pollutant emissions. However, as in every process of energy production, a gas-steam unit also produces wastes and the need for their utilization. For this reason, it is necessary to assess the business potential of new technologies before their implementation.

Coal-based gas-steam plants with integrated fuel gasification are not yet fully commercial. The slags resulting from coal gasification are relatively new and poorly recognized. They are produced in only 18 plants worldwide (Pérez-Fortes et al. 2009).

As described in existing documentation, the slags produced during coal gasification processes are characterized by a high content of SiO_2 from about 40 to 47%, and Al_2O_3 from about 11 to 29% (Table 1). The content of CaO is characterized by high variation and varies from 9 to 26%.

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* Prof., ** Ph.D., *** D.Sc., AGH University of Science and Technology, Krakow, Poland;
e-mail: mamaz@agh.edu.pl

TABLE 1

The chemical composition of the slags from different gas-steam plants with integrated fuel gasification

TABELA 1

Skład chemiczny żużli z różnych instalacji bloku gazowo-parowego ze zintegrowanym zgazowaniem paliwa

Chemical component	Chemical composition of slags according to different authors		
	Song et al. 2010a	Song et al. 2010b	Tang et al. 2010
LOI (1000°C)	–	–	25,69
SiO_2	41.16	46.55	40.83
Al_2O_3	15.69	26.04	11.76
Fe_2O_3	12.60	3.30	6.46
TiO_2	0.77	1.14	
CaO	26.04	20.58	9.36
MgO	1.34	0.96	1.04
SO_3	–	0.23	0.72
Na_2O	1.39	0.33	1.20
K_2O	1.01	0.87	1.75

Currently, studies are focusing on the utilization of wastes. It has been shown that slags resulting from gasification might be used as raw material for brick production (Acosta et al. 2002) and as porous, lightweight aggregate (Aineto et al. 2005). It has been also found that slag can be used as a pozzolanic material (Acosta et al. 2002).

As mentioned, slags are also produced in underground coal gasification – though this has not described in scientific documentation. Presently, there are many underground coal gasification pilot plants worldwide (Stanczyk et al. 2011).

Using wastes from power production as building materials has been the basic trend in their utilization in Poland for many years. For this reason, the major method of wastes utilization resulting from gasification processes is as a pozzolanic material for cement production.

This paper presents the pozzolanic properties of two types of slags – from currently operating coal gasification and from underground coal gasification. The impact of additional grinding of the slags on their pozzolanic reactivity has been also analyzed.

2. Characterization of the slags

In this examination, the slags from two coal gasification plants were used (Stanczyk et al. 2011, 2012). The slag from the gas-steam plant with integrated fuel gasification was denoted as MI, and the slag from the underground coal gasification pilot plant was named BA.

The chemical compositions of the slags are presented in Table 2, and their grain size distribution in Table 3 and Figure 1. For the competent characteristics of the slags, phase composition analysis has been performed.

Table 2 shows that slag MI can be classified as basic slag with a chemical composition similar to silica fly ash from coal combustion. Slag BA – because of its four times higher content of calcium oxide (at around 19.0%) – belongs to a group of weakly basic slags. The high content of CaO in slag BA, with high Al_2O_3 content, points to the greater hydraulic activity of this material (activity module M_a is 0.68).

TABLE 2

Chemical composition of the slags [wt%]

TABELA 2

Skład chemiczny żużli [%wag.]

Chemical component	Sample	
	BA	MI
LOI (1000°C)	0.66[1]	0.15
SiO_2	51.10	55.40
Al_2O_3	16.90	26.80
Fe_2O_3	8.30	5.90
TiO_2	0.65	1.00
CaO	19.00	4.60
MgO	1.80	1.90
S^{2-}	0.05	0.05
SO_3	0.08	0.09
Na_2O	0.65	0.25
K_2O	1.40	3.11
S	99.93	99.25

1) sample roasting started the oxidation process: $Fe^{2} + \rightarrow Fe^{3+}$

TABLE 3

Particle size distribution of slag [vol.%]

TABELA 3

Skład ziarnowy żużli [%obj.]

Sample	Size fraction of material				
	< 5 µm	5–15 µm	15–45 µm	45–63 µm	>63 µm
BA	6.4	9.0	23.6	13.6	47.4
MI	10.2	12.4	31.1	15.6	30.7

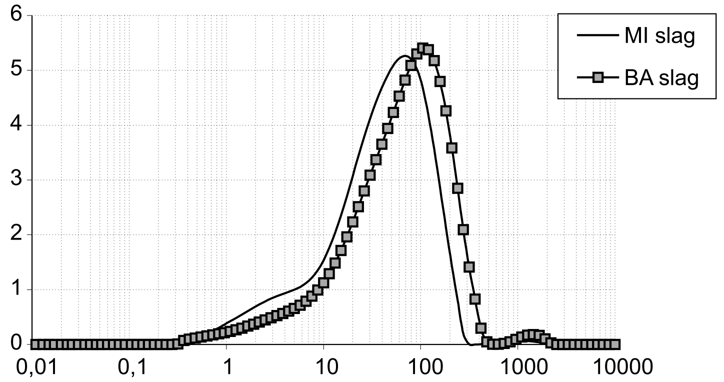

Fig. 1. Grain size distribution curves of the slags

Rys. 1. Krzywa uziarnienia żużli

The grain size analysis shows that slag MI is finer in relation to slag BA. The content of selected grain size fractions smaller than 15 mm is 10.2% for slag MI and 6.4% for slag BA. The total content of particles smaller than 45 mm stands at 53.7 and 39.0% for MI and BA respectively. The amount of particles larger than 63 mm in slag BA is 47.4% and is 50% higher than for slag MI.

The X-ray diffraction patterns of the slags are presented in Figures 2 and 3.

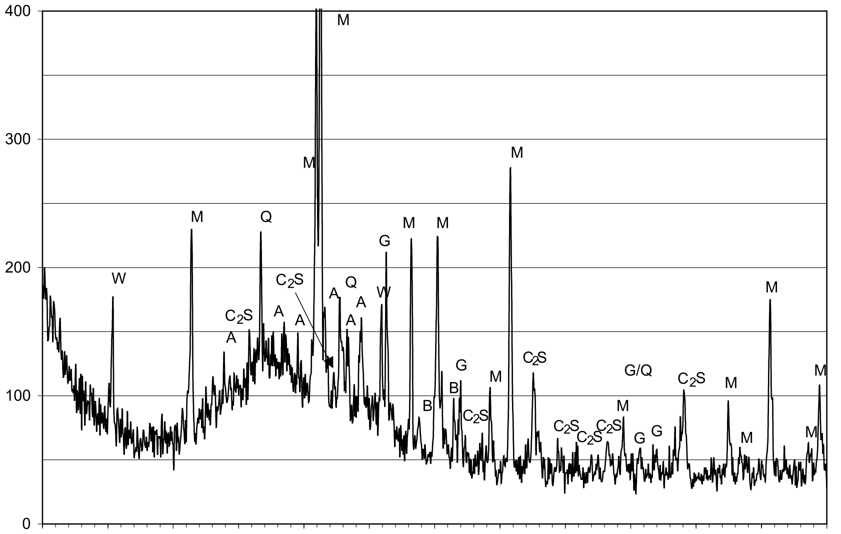

Fig. 2. X-ray diffraction pattern of slag BA: Q – β SiO_2, M – mullite, A – anorthite, G – gehlenite, W – wollastonite $CaO \cdot SiO_2$, C_2S – $2CaO \cdot SiO_2$, B – $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

Rys. 2. Dyfraktogram rentgenowski żużla BA: Q – β SiO_2, M – mullit, A – anortyt, G – gehlenit, W – wollastonit $CaO \cdot SiO_2$, C_2S – $2CaO \cdot SiO_2$, B – $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$

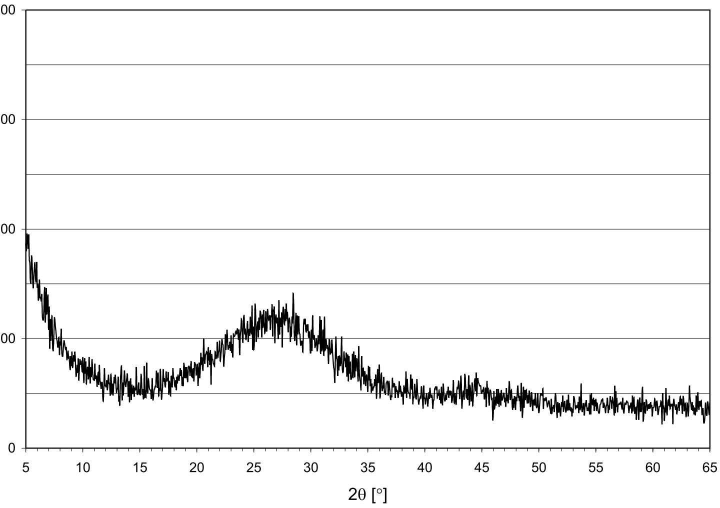

Fig. 3. X-ray diffraction pattern of slag MI

Rys. 3. Dyfraktogram rentgenowski żużla MI

The X-ray analysis shows a characteristic increase in the background at the 2 θ angle in the range between 15° and 40° (Figure 2 and 3). The main and only mineral component in slag MI is glassy phase, which is confirmed by the studies of other authors (Acosta et al. 2001, 2002; Aineto et al. 2006; Song et al. 2010a, b). Slag BA contains – besides the glassy phase – crystalline phases, namely mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$), quartz ($\beta$-$SiO_2$), anorthite ($Ca(Al_2Si_2O_8)$), gehlenite ($Ca_2Al[(Si,Al)_2O_7]$), wollastonite ($Ca_3[Si_3O_9]$), $2CaO \cdot SiO_2$,

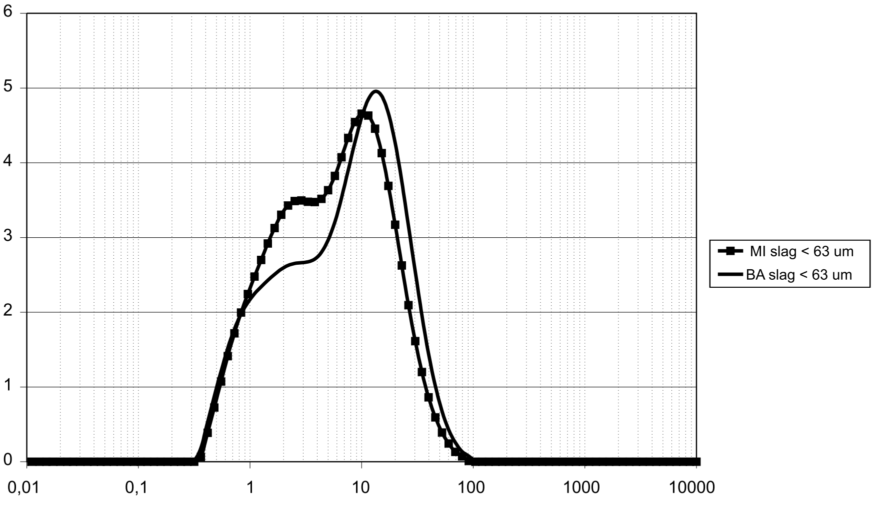

Fig. 4. Particle size distribution of the slags after grinding and sieving through a 63 μm sieve

Rys. 4. Skład ziarnowy żużli po domieleniu i przesianiu przez sito 63 μm and 4 CaO · Al_2O_3 · Fe_2O_3. The presence of crystalline minerals in the form of gehlenite indicates a slightly alkaline nature of the slag.

In order to study the impact of particle size of slags on their pozzolanic activity, the samples were ground and sieved through a 63 mm sieve. Particle size distribution of the slags after grinding and selection of the fraction below 63 mm is shown in Figure 4.

3. Pozzolanic activity of the slags

The pozzolanic activity of the slags was performed according to the standard ASTM C379-65T Specification for Fly Ash for Use as a Pozzolanic Material with Lime. The results are shown in Table 4 and Table 5. This method is based on a determination of the sample's total content of silica and alumina soluble in NaOH and therefore potentially reactive with calcium hydroxide. The content of active SiO_2 and Al_2O_3 in the material correlates with the results of strength measurements of cement mortars.

The usefulness of waste materials as an additive in the cement and concrete industry depends on their pozzolanic properties. The pozzolanic activity is determined by the content of active SiO_2 and Al_2O_3, whose increase indicates an increased pozzolanic character of the

TABLE 4

Pozzolanic activity of the slags from coal gasification according to the standard ASTM C379-65T [wt%]

TABELA 4

Aktywność pucolanowa żużli ze zgazowania węgla według normy ASTM C379-65T [%wag.]

Sample	Active chemical component		
	SiO_2	Al_2O_3	$SiO_2 + Al_2O_3$
BA	6.1	1.0	7.1
MI	4.9	1.8	6.7

TABLE 5

Pozzolanic activity of the fraction below 63 μm of the slags from coal gasification according to the standard ASTM C379-65T [wt%]

TABELA 5

Aktywność pucolanowa żużli ze zgazowania węgla według normy ASTM C379-65T [%wag.]

Sample	Active chemical component		
	SiO_2	Al_2O_3	$SiO_2 + Al_2O_3$
BA after grinding < 63mm	14.1	3.0	17.1
MI after grinding < 63mm	9.6	5.2	14.8

material (Kurdowski 2010). The material can be classified as a good pozzolan when the reactive SiO_2 content is above 25% (BS EN 197-1: 2002).

The results show that slag BA (from underground coal gasification) has a better pozzolanic activity than slag MI (from the gas-steam plant with integrated fuel gasification). The difference in the content of the active components (SiO_2 and Al_2O_3) in the slags is up to 6.0%. The increase in the reactivity of slag BA is associated with the presence of a few percent of crystalline minerals in the form of active calcium aluminosilicate, especially gehlenite.

The additional grinding of the slags resulted in an increase in the total content of active chemical components (SiO_2 and Al_2O_3) of 14.8% for slag MI and of 17.1% for slag BA (Table 5). It means that pozzolanic activity of the fraction below 63 μm of both slags has increased two times when compared with the original samples. The greater increase in the content of active components in the case of slag BA can be connected with the larger amount of active crystalline phases in its finer fraction.

However, despite an increase in the content of active silica and alumina, the slags cannot be qualified as a pozzolanic material for cement and concrete.

For a full characterization of the pozzolanic activity of the slags, the pozzolanic activity index has been determined according to the standard PN-EN 450-1:2009 Fly ash for concrete. Part 1: Definitions, specifications, and compatibility criteria. The composition of the mixtures was consistent with the standard and was 75wt.% Portland cement CEM I 42.5R and 25wt.% slag sample. The water-cement ratio was 0.28. The compressive strength of the cement mortars was determined under hydrothermal conditions (steam curing temperature of 80°C) according to the following cycle:

- the initial maturation of the samples – 3 h,
- the heating time of the samples at 80°C – 2.6 h,
- the steam curing of the samples at 80°C – 4 h,
- the cooling time of the samples at 25°C – 12 h.

TABLE 6

Compressive strength of cement mortars with the addition of the slags from coal gasification

TABELA 6

Wytrzymałość na ściskanie zapraw cementowych z dodatkiem żużli ze zgazowania węgla

Sample	Compressive strength [MPa]			Pozzolanic activity index [%]	
	hydrothermal conditions (80°C)	after 28 days of storage in water	after 90 days of storage in water	after 28 days	after 90 days
CEM I 42.5R	59.8	83.3	111.0	–	–
75wt.% CEM I 42.5R + + 25wt.% slag MI	49.8	69.5	77.6	83.4	69.9
75wt.% CEM I 42.5R + + 25wt.% slag BA	49.0	71.8	83.4	86.2	75.1

After the steam curing, the samples were put in water (at a temperature of 25°C). After 28 and 90 days of storage in water, compressive strength of the cement mortars was determined again. The results are summarized in Table 6.

According to PN-EN 450-1:2009, the material can be classified as a pozzolana if the pozzolanic activity index is not less than 75% after 28 days and 85% after 90 days. The slags show a high value of the pozzolanic activity index – more than 80% – after 28 days (respectively 83.4% for slag MI and 86.2% for slag BA). However, after 90 days, the rate of increase in compressive strength is lower and the pozzolanic activity index is about 70% (respectively 69.9% for slag MI and 75.1% for slag type BA). This is caused by the weak pozzolanic properties of the slags, especially slag MI, and consequently by slight increases in the compressive strength of cement mortars after a long period of time.

Conclusion

The implementation of coal gasification technology will create a new type of waste that should be utilized. Currently, coal-based gasification plants – although not fully commercial – are working and producing wastes. Based on the study of these wastes, it is not possible to determine directions for the utilization of waste formed in coal-based gasification technology. This applies to both gas-steam plants with integrated fuel gasification and underground gasification. The results presented in this paper suggest that these wastes do not have the desired pozzolanic properties. However, the waste produced in existing plants reveal different chemical and phase compositions, primarily due to the use of various technologies as well as the use of various coal types. Therefore, the application of the slags from coal gasification in cement and concrete production requires further study. The analysis of only two slag types is obviously insufficient to fully answer the question. As a consequence, it cannot be clearly concluded whether the resulting waste could or could not be used as a pozzolanic additive in cement or concrete after the introduction of this technology in Poland.

The presented results of research have been developed under the framework of the research project of the Ministry of Science and Higher Education, No. N N524 361038: Studies of slags resulting from high temperature coal gasification plants in terms of their use in mining technologies

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WSTĘPNE OKREŚLENIE PRZYDATNOŚCI ŻUŻLI ZE ZGAZOWANIA WĘGLA JAKO SUROWCA PUCOLANOWEGO

Słowa kluczowe

Żużle ze zgazowania, skład chemiczny, skład granulometryczny, aktywność pucolanowa, wytrzymałość na ściskanie

Streszczenie

Wymagania dotyczące ochrony środowiska, takie jak: ograniczenie emisji CO_2, NO_x i SO_2 spowodowały coraz większe zainteresowanie nowymi technologiami energetycznego wykorzystania węgla. Jedną z testowanych i promowanych obecnie technologii jest zgazowanie węgla. Jednak, jak każda technologia produkcji energii wykorzystująca węgiel, powoduje ona powstawanie odpadów: popiołów lotnych i żużli. Ze względu na niewielką ilość instalacji zgazowania węgla funkcjonujących obecnie w świecie, odpady te są w niewielkim stopniu poznane, dlatego też przed podjęciem decyzji o wprowadzaniu technologii zgazowania węgla, powinno się opracować technologię utylizacji powstających w niej odpadów. Najlepszym rozwiązaniem będzie oczywiście opracowanie kierunku ich gospodarczego wykorzystania. Jedną z możliwości rozpatrywanych dla gospodarczego wykorzystania żużli ze zgazowania jest zastosowanie ich jako składnika spoiw mineralnych o charakterze pucolanowym.

W artykule przedstawiono wyniki badań aktywności pucolanowej dwóch żużli: żużla ze zgazowania węgla z instalacji energetycznego zgazowania oraz podziemnego zgazowania. Ze względu na skład chemiczny żużel MI można zaklasyfikować jako żużel zasadowy o składzie chemicznym zbliżonym do krzemionkowego popiołu lotnego ze spalania węgla kamiennego. Z kolei żużel BA, z powodu czterokrotnie wyższej zawartości tlenku wapnia, należy do grupy żużli słabozasadowych. Podstawowym i jedynym składnikiem mineralnym żużla MI jest faza szklista. W żużlu BA, obok fazy szklistej, tworzą się również fazy krystaliczne, a mianowicie:

mullit 3 $Al_2O_3 \cdot 2\ SiO_2$, kwarc β-SiO_2, anortyt $Ca(Al_2Si_2O_8)$, gehlenit $Ca_2Al[(Si,Al)_2O_7]$, wollastonit $Ca_3[Si_3O_9]$, $2CaO \cdot SiO_2$ i $4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$. W wyniku badań stwierdzono, że żużel BA wykazuje większe wartości wskaźnika aktywności pucolanowej (75,1% po 90 dniach) od żużla MI (69,9% po 90 dniach). Niestety, wstępne badania pozwalają stwierdzić, że żużle te charakteryzują się zbyt niską aktywnością pucolanową i nie mogą być traktowane jako materiał pucolanowy w technologii produkcji cementu i betonu.

PRELIMINARY DETERMINATION OF THE SUITABILITY OF SLAGS RESULTING FROM COAL GASIFICATION AS A POZZOLANIC RAW MATERIAL

Key words

Slags resulting from underground coal gasification, slags resulting from fuel (coal) gasification plant, chemical composition, granulometric composition, pozzolanic activity

Abstract

Requirements for environmental protection, such as reducing emissions of CO_2, NO_x, and SO_2 are the reason for growing interest in new technologies for coal utilization. One of the most promoted technologies is coal gasification. However, like any technology using coal, this process produces wastes – fly ash and slag. Due to the small number of coal gasification plants, these wastes are poorly understood. Therefore, before making decisions on the introduction of coal gasification technology, a waste utilization plan should be developed. This also applies to the slags formed in underground coal gasification technology. One of the options under consideration is to use these wastes as a component in mineral binders of a pozzolanic character. This paper compares the properties of two types of slags. The first slag (MI) comes from fuel gasification, and the second slag (BA) is from underground coal gasification. Slag MI can be classified as basic slag with a chemical composition similar to that of silica fly ash from coal combustion. Slag BA – because of its four times greater content of calcium oxide – belongs to a group of weakly basic slags. The main and only mineral component of slag MI is glassy phase. Slag BA forms – besides the glassy phase – crystalline phases such as mullite ($3\ Al_2O_3 \cdot 2\ SiO_2$), quartz ($\beta$-$SiO_2$), anorthite ($Ca(Al_2Si_2O_8)$), gehlenit ($Ca_2Al[(Si,Al)_2O_7]$), wollastonite ($Ca_3[Si_3O_9]$), $2CaO \cdot SiO_2$, and $4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$. The results of analyses have shown that slag BA has better pozzolanic properties (the pozzolanic activity index is 75.1% at 90 days) than slag MI (69.9% at 90 days) The preliminary studies lead to the conclusion that these slags are characterized by very low pozzolanic activity and cannot be used as a pozzolanic material.