www.ees.uni.opole.pl
ISSN paper version 1642-2597
ISSN electronic version 2081-8319
Economic and Environmental Studies
Vol. 17, No. 3 (43/2017), 613-624, September 2017

The Role of the Granulated Blast Furnace Slag in Sustainable Cement Production and Waste Management

Anna KRÓL
Opole University of Technology, Poland

Abstract: Sustainable development is a call to prudence and moderation efforts to reconcile key areas for humanity: ecological, economic and social development. Consistent with the idea of sustainable development is the use of by-products from other industries for the production of clinker, cement and concrete. These products can successfully replace natural minerals or clinker in cement production. This considerably reduces the extraction of natural resources and increases the economy of the process, without compromising the quality of the product. In cement production technology increasingly important role starts to play also active mineral additives. In the world's cement production process it has economic, ecological, but also technological base. The aim is in fact to obtain such cements whose properties will receive high durability concrete, and the use of suitable mineral supplements can be helpful in this. Known mineral additive is granulated blast furnace slag - waste coming from the steel industry. This material is increasingly being used also in the process of solidification of hazardous waste. The use of granulated blast furnace slag in the cement industry and in the process of solidification of galvanic sludge is presented in the paper with the presentation of the author's own research in this field.

Keywords: granulated blast furnace slag, waste management, cement production, solidification, heavy metals

JEL codes: L61, Q42

https://doi.org/10.25167/ees.2017.43.10

1. Introduction

The idea of sustainable development is to set up sustainable economic and social progress harmonized with the protection of environment. It is the pursuit of building an economic model that will ensure the progress of humanity without destroying the supporting systems of nature. This means the use of natural goods while respecting them. Sustainable development does not stand in

Correspondence Address: Anna Król, Department of Environmental Engineering, Faculty of Mechanical Engineering, Opole University of Technology, 5 Mikolajczyka Str., 45-271 Opole, Poland. Tel.: +48 77 4498385 E-mail: a.krol@po.opole.pl

a contradiction to progress. It is, however, a call to maintain prudence and moderation aimed at reconciling the areas of ecological, economic and social importance for humanity (Pawłowski et al., 2004).

The use of by-products from other industries to produce clinker, cement or concrete is also consistent with the concept of sustainable development. These products can successfully replace natural minerals or clinker in cement production. This significantly limits the extraction of natural raw materials and raises the economy of the process without compromising the quality of the product (Pawłowski et al., 2004).

Consistent with the idea of sustainable development is the use of alternative fuels in the Portland clinker production. Most waste, with the right minimum energy value, can be used to produce alternative fuels. The use of alternative fuels in the cement industry has a positive effect on the economics of the clinker production process, moreover, it increases the ecological effects of fuel combustion (such as reducing emissions of gases and dust into the atmosphere). Cement kilns are one of the few industrial installations in which waste fuels are used as a component of a traditional fuels. Co-combustion of alternative fuels with fossil fuels is an effective, safe for environment action that integrates into the energy recovery process (Wzorek and Król, 2009: 132-136; Wzorek and Król, 2012: 444-465). The consumption of alternative fuels in the cement industry in Poland amounted to 1180.5 thousand Mg.

The substitution of clinker with active mineral additives is becoming a more important factor in the technology of cement production. In global cement production, this process has both economic and ecological but also technological background. It is indeed striving to obtain such cements, which will provide high durability concrete, and the use of suitable mineral additives may be of help here (Roskovic' and Bjegovic', 2005: 974-978).

Mineral additives for cement are mainly the by-products of combustion from the power industry and waste generated in the steel industry, i.e. siliceous fly ash (referred to as V in cement name). and granulated blast furnace slag (referred to as S). (PN-EN 15167; 197; PN-EN 450). These are the materials characterized by pozzolanic and/or hydraulic activity. Gypsum, applied in the amount of 4 to 6% of cement mass as a binding time regulator, acts an important factor in the balance of mineral additives used for cement. This role is in most cases performed by gypsum from flue gas desulphurisation from power industry boilers (often called reagypsum).

In recent years, interest in the cement industry has also been directed towards limestone fly ash (W). derived from the brown coal combustion (Giergiczny, 2006, Ponikiewski T. et al., 2012, Navarro-Blasco I. et al., 2013:89-103).

According to the Association of Cement Producers (Bulletin 2016), more than 4 200 thousand Mg of secondary raw materials, including almost 1 400 thousand Mg of blast furnace slags, was used for cement in the Polish cement industry in 2012.

The activity of the cement industry is therefore of benefit to the environment. The production of clinker and cement employs the consumption of by-products from other industries, thus, eliminating waste from the environment while preserving reserves of raw materials or fossil fuels.

In addition, the development of technology aims at the wide use of mineral binders for the disposal of hazardous waste through the process of solidification/stabilization (s/s). This method was developed in the middle of last century to neutralize radioactive waste. Over time it has been adapted for the disposal of other, particularly industrial and hazardous waste or sewage sludge. The process of solidification allows the physical and chemical properties of the waste to be altered, furthermore, to reduce solubility and leaching of dangerous compounds (Król, 2007: 971-973, Król, 2012: 29-40). In order to permanently solidify the waste in mortars or concretes, cements of ordinary use are applied in accordance with the requirements of the standard (PN-EN 197), but also mineral binders of a different composition, which are based in particular on mineral additives.

The article emphases the use of granulated blast furnace slag in the production of binders to effectively solidify hazardous industrial waste. The aim of this paper is to present the results of own research focusing on the assessment of the environmental impact and durability of composites used for the stabilization of hazardous waste.

2. Granulated blast furnace slags as a material for the sustainable production of cement and mineral binders

The consumption of mineral additives in cement production increased in Poland in last 10 years more than double. Socio-economic considerations allow for a further increase in the use of mineral waste as an additive to cement, thereby reducing CO_2 emissions, reducing cement production costs and the cost of waste storage (Baran et al., 2010: 22-25). Giergiczny (2008: 105-122). assumes, that the highest level of CO_2 emission appears during the production of Portland cement CEM I

(766 kg/Mg of cement), whereas the lowest, while producing metallurgical cement CEM III/B 32,5L-LH-HSR/NA, in which the content of granulated blast furnace slag is 75% (216 kg / Mg of cement). The amount of cement clinker production must be realized taking into account the CO_2 emission allocations, and therefore the increase of mineral additives in the cement composition and the reduction of the clinker share is a key solution to significantly reduce the carbon footprint of the cement industry. Consequently, changes in assortment can be observed in domestic cement production. For example, as for the years 1999-2005, the share of CEM I Portland cement in the sales structure was 46 - 47.9%; in 2007 it decreased to 37.6% and this share is steadily decreasing each year.

The wide availability of cements with additives (CEM II ÷ CEM V). results in their increasing use as binders in the production of small- and large-size precast elements, as well as in the production of new-generation concrete (Giergiczny et al., 2002). Cements with a high content of mineral additives, especially fly ash and/or granulated blast furnace slag, are characterized by low hydration heat and high resistance to chemical aggression. These cements are the component of, for example, solid mass concrete (CEM III applied with low hydration heat LH). or sewage treatment plants (blended cements HSR sulphate resistant and with lower hydration heat HS). (Giergiczny, 2008). Thus, the production of cements with additives brings not only ecological and economic benefits, but it is also the construction of durable building structures resistant to various types of aggressive chemical environments.

Mineral additives have also a positive effect on the structure and properties of the mineral materials being produced. The presence of granulated blast furnace slag in binder structures improves the properties of binder matrixes, among others through the following (Giergiczny et al., 2002): (i) reduction of the permeability of slag composites (associated with reduced porosity and the formation of more gel pores, which prevents the ingress of liquid into the hardened structures), (ii) improved resistance to aggressive factors (due to low $Ca(OH)_2$ content in pastes, (iii) increased compressive strength of materials made with the addition of granulated blast furnace slag in longer setting periods.

In general, modern construction and building materials, in the context of sustainable development, should be seen in the light of minimal impact of the construction process and the use of building objects on environment, and so, the facilities can be healthy and safe for users (Ajdukiewicz, 2004: 38-44).

3. The advantages of using granulated blast furnace slag in solidification of hazardous waste

Considering the above described advantages of granulated blast furnace slag in the formation of durable mineral composite structures, it can be concluded that this material may also be suitable for the production of matrices solidifying hazardous industrial waste.

Solidification of cementitious materials makes it possible to change the physical characteristics of the waste, since the accomplished waste material with limited (usually small). liquid phase content is mainly responsible for the transport of harmful substances into the environment.

The efficiency of the solidification process in cement matrices is determined by the two features: matrix durability and heavy metal leaching (Król and Jagoda, 2012: 90-101; Batchelor, 2006: 689-698; Malviya and Chaudhary, 2006: 267-276). Unfortunately, these two features are characterized by many other parameters, and therefore the unambiguous evaluation of the solidifying composite is very difficult. The durability of the matrix itself, for example, includes strength, water absorption, depth of penetration, porosity. And it is well known, that concrete that solidify hazardous waste stored in the environment or used as aggregates or granules in engineering construction may be exposed to various adverse of environmental conditions (Fitch and Cheeseman, 2003: 239-255).

The objective of using granulated blast furnace slags from the metallurgical industry for the manufacture of composites solidifying hazardous waste is to obtain matrices of an increased durability. These slags are also to support the process of heavy metals retention (immobilization). in the composite.

4. Materials and methods

Concrete tests were designed and executed using the following cements:

- Portland cement CEM I 32.5R (hereinafter referred to as CEM I);
- Slag cement CEM III/B 32,5N-LH-HSR/NA, in which the content of granulated blast furnace slag was 75% (hereinafter referred to as CEM III/B).

The content of heavy metals and blast furnace slag used in cements for the tests purposes is presented in Table 1.

The composition of concrete mix was as follows: cement – 300.0 kg/m^3; sand – 685.2

kg/m^3; gravel 2÷8 mm – 600.4 kg/m^3; gravel 8÷16 mm – 628.6 kg/m^3; water – 180.0 kg/m^3; water/cement ratio (w/c). in all mixtures – 0.6. Such prepared mixtures were the reference samples. In addition, samples were made in which 10% of cement was replaced with hazardous waste– galvanic sewage sludge (GO). The heavy metals content in the waste is shown in Table 2.

Concrete blocks of 10x10x10 cm were formed out of provided mixture. After 24 hours, the cubes were subjected to a leaching test or a physico-mechanical tests.

Eluates from concrete samples or waste were carried out according to PN-EN 12457. According to the procedure described, the test material of particle size <10 mm was shaken with water for 24 hours while maintaining a water to solid ratio (L/S). equal to 10.

The heavy metal content of the eluates was determined by atomic absorption spectrometry.

The pore size distribution in the samples was made using a PoreMaster 60 mercury porosimeter. The measurements were made in the range of 3.5 nano- to 10 micrometers.

Compressive strength of concrete was determined according to PN-EN 12390.

Table 1. The content of selected heavy metals in cements and granulated blast furnace slag

Heavy metal	**Content [mg/kg]**		
	CEM I	**CEM III/B**	**Granulated blast furnace slag**
Cr	54	31	12
Zn	316	105	36
Cd	< 1	< 1	3
Pb	24	39	<5
Co	7	3	6
Ni	18	11	<2.5
Mn	288	1638	1978
V	34	31	10
Cu	60	27	22
As	6	0.3	5
Hg	< 0.08	0.08	3.5
Tl	< 5	<5	22

Source: own research

Table 2. The content of heavy metals in dry mass of galvanic sewage sludge (GO)

Heavy metal	Content [mg/kg]
Cr	270100.7
Zn	1441.1
Cd	1133.5
Pb	545.8
Co	163.7
Ni	12789.6
Mn	140.2
V	185.6
Cu	38443.5
As	20.5
Hg	31.8
Tl	0.234

Source: own research

5. Results and discussion

The waste selected for testing cannot be counted as an inert waste. In the eluates, significant concentrations of heavy metals such as chromium, nickel and cadmium were observed (Table 3). as compared to permissible metal concentrations in the water extracts from waste deposited on inert waste landfills (Regulation of the Minister 2013).

Hazardous waste prior to the deposit in the environment is often subjected to a solidification process. This greatly allows the reduction of leaching of heavy metals to water or soils.

Table 3. The content of heavy metals in eluates from galvanic sewage sludge (GO)

Heavy metal	Concentration in eluate [mg/kg]	Limit values acc. to the Regulation (2013). for eluates from waste [mg/kg]	
		Inert waste	Non-hazardous and inert waste
Cr	3.04	0.5	10.0
Zn	0.44	4.0	50.0
Cd	0.71	0.04	1.0
Pb	0.017	0.5	10.0
Co	0.64	-	-
Ni	8.86	0.4	10.0
Mn	6.54	-	-
V	0.030	-	-
Cu	0.48	2.0	50.0
As	0.015	0.5	2.0
Hg	0.0053	0.01	0.2
Tl	0.0027	-	-

Source: own research

The results obtained from the immobilization of heavy metals from galvanic sewage sludge in matrices made of Portland cement as well as of slag cement were determined in two research environments. Some of the tests were exposed to the annual environmental impact, and some were left in continuous contact with distilled water for the same period. The resulting concentrations of selected heavy metals are shown in Table 4.

Table 4. Leaching of selected heavy metals from concrete samples solidifying hazardous waste (GO) exposed to different research environments for over a year

Environment of concrete samples exposure	Sample designation	Concentration of heavy metals [mg/dm^3] in water eluates					
		Cr	**Zn**	**Ni**	**Cu**	**Cd**	**Pb**
Distilled water	CEM I+GO	0.054	0.021	0.002	0.020	0.0001	0.005
	CEM III/B*+GO	0.205	0.025	0.013	0.015	0.0022	0.024
Natural environment	CEM I+GO	0.186	0.001	0.020	0.006	0.001	0.044
	CEM III/B*+GO	0.240	0.001	0.011	0.006	<0.001	0.032

* cement with 75% content of granulated blast furnace slag
Source: own research

The obtained leaching levels are low and the concrete mixtures used allow to significantly reduce the leachability of heavy metals. It should be noted that slag cement compared to Portland cement increases the level of immobilization of heavy metals (e.g. Ni, Pb when matrices are exposed in the natural environment). Habib M.A. et al., 2012: 263-269 and Song F. et al, 2013: 344-350 had also such observations.

Reduction of heavy metals leaching can be the result of changes in the microstructure of pastes. The addition of granulated blast furnace slag reduces the overall porosity of CEM III/B samples compared to CEM I (from 10.32% to 7.66%). moreover, it allows to reduces the average pore size from 0,105 to 0,014 μm (gel pore limit). It is important when considering the limitations in heavy metal leaching. Gel pores are among the group of closed pores, which prevents the liquid from flowing outside the matrix. Matrices for the disposal of hazardous waste must perform a high degree of durability in the environment. This feature is determined in particular by the compressive strength of such composites. Those researches are in consistent with Neville's A.M (2012).

In the course of the tests the strength of concrete samples with the addition of hazardous waste was assessed. The tests were performed both for samples stored in distilled water and for samples exposed to the atmospheric environment for one year.

The results of strength tests presented in Table 5 prove that cement with the addition of blast furnace slag (CEM III/B). does not only maintain similar strength to Portland cement with samples exposed to the environment, but also is characterized by get much higher strength when the samples are continuously subjected to water throughout one year. This demonstrates the high durability of such matrices and greater assurance of the stability of the solidification process under different exposure conditions.

Table 5. Compressive strength of samples stored in different environments during 1 year

Concrete designation	**Storing environment**	**Compressive strength [MPa]**
CEM I+GO	Natural environment	40.3
	Distilled water	40.6
CEM III/B*+GO	Natural environment	37.8
	Distilled water	48.9

* cement with 75% of granulated blast furnace slag
Source: own research

6. Conclusion

The management of hazardous waste is a challenge for all communities, and therefore becomes an extremely important part of the global environment. This system requires the methods and processes used are in line with the pillars of sustainability. Waste management should hence be designed and executed in a way to protect the environment and, where possible, use other by-products in the disposal process. The solidification/stabilization method of waste disposal is such an example. The disposal of hazardous waste applies to both cements of common use and by-products of the steel industry, such as granulated blast furnace slag (Müllauer W., 2015: 129-139). Due to the use of blast furnace slag, it is possible to limit the application of Portland cement, which is energy intensive and expensive in production.

The results presented in the article indicate that the use of granulated blast furnace slag in solidified sewage sludge is a correct and even a desirable action. This will allow to achieve matrices with increased gel pore content, limiting the release of pore liquid into the natural environment. The transport of liquids containing heavy metals from waste is thereby being reduced. This leads to an increase in the level of immobilization of heavy metals in solidifying composites containing slags. An additional advantage is also the increase in the strength of slag containing matrices compared to matrieces made of CEM I (Portland cement).

Granulated blast furnace slag give therefore raise hope and the opportunity to run the process of solidifying hazardous waste in a sustainable way and with the preservation of the environment. The use of granulated blast furnace slag in this process is consistent with the idea of sustainable waste management. The results of the presented research are of great importance for the developing hazardous waste management sector based on stabilization in mineral composites.

Literature

Ajdukiewicz, A. (2004). Beton a rozwój zrównoważony (Concrete and Sustainable Development). *Budownictwo Technologie Architektura*, 4:38-44

Bapat ,J.D. (2001). Performance of cement concrete with mineral admixtures. *Advances in Cement Research* vol. 13: 139-155

Baran, T.; Pichniarczyk, P.; Kalarus, D. (2010). Ograniczanie emisji gazów i pyłów – wykorzystanie odpadów w przemyśle (Reduction of gas and dust emissions - use of waste in industry). *Izolacje*. 5: 22-25

Batchelor, B. (2006). Overview of waste stabilization with cement. *Waste Management* 26: 689-698

Berndt, M.L. (2009). Properties of sustainable concrete containing fly ash, slag and recycled concrete aggregate. *Construction and Building Materials*, vol. 23: 2606–2613

Biuletyn Stowarzyszenia Producentów Cementu (Association of Cement Producers Bulletin). 2016.

Fitch, J.R.; Cheeseman C.R. (2003). Characterisation of environmentally exposed cement-based stabilised/solidified industrial waste. *Journal of Hazardous Materials* vol. A101: 239–255

Fu, X.; Wang, Z.; Tao, W.; Yang, Ch.; Hou, W.; Dong, Y.; Wu, X. (2002). Studies on blended cement with a large amount of fly ash. *Cement and Concrete Research* 32: 1153-1159

Giergiczny, Z.; Małolepszy, J.; Szwabowski, J.; Śliwiński, J. (2002). Cementy z dodatkami mineralnymi w technologii betonów nowej generacji (Cements with mineral additives in new generation concrete technology). Opole: Wydawnictwo Instytut Śląski.

Giergiczny, Z. (2006). *Rola popiołów lotnych wapniowych i krzemionkowych w kształtowaniu właściwości współczesnych spoiw budowlanych i tworzyw cementowych (The role of calcium and silica fly ash in shaping the properties of modern building matrieces)*. Monografia 325. Kraków: Politechnika Krakowska.

Giergiczny, Z. (2008). Zrównoważony rozwój a produkcja cementu (Sustainable development and cement production). KILiW PAN Problemy naukowo-badawcze Budownictwa T.IV Zrównoważony rozwój w budownictwie (54 Konferencja Naukowa), Krynica-Białystok, 105-122.

Habib, M.A.; Bahadur, N.M.; Mahmood, A.J.; Islam, M.A, (2012). Immobilization of heavy metals in cementitious matrices. *Journal of Saudi Chemical Society* 16: 263-269

Król, A. (2007). Wiązanie jonów chromu w procesie hydratacji spoiw mineralnych (Binding of chromium ions in hydration of mineral binders). *Przemysł Chemiczny* 10: 971-973

Król, A. (2012). Durability of stabilised galvanic sewage sludge against the impact of sea water and sulphate solution. *Environmental Protection Engineering* 4 (vol.38): 29-40

Król, A.; Jagoda, D. (2012). Carbonation and the durability of cement composites immobilizing heavy metals. *Cement Wapno Beton*, 2: 90-101

Malviya, R.; Chaudhary, R. (2006). Factors affecting hazardous waste solidification/stabilization: A review. *Journal of Hazardous Materials* B137: 267–276

Müllauer, W.; Beddoe, R.E.; Heinz, D. (2015). Leaching behaviour of major and trace elements from concrete: Effect of fly ash and GGBS. *Cement and Concrete Composites* 58: 129-139

Navarro-Blasco, I.; Duran, A.; Sirera, R.; Fernandez, J.M.; Alvarez, J.I. (2013). Solidification/stabilization of toxic metals in calcium aluminate cement matrices. *Journal of Hazardous Materials* 260: 89-103

Neville, A.M. (2012). Properties of concrete. SPC. Kraków

Pawłowski, A. et al. (2004). *Realizacja zasady zrównoważonego rozwoju w przemyśle cementowym (Implementation of the principle of sustainable development in the cement industry).* In: *Ochrona i inżynieria środowiska*. Monographs of the Committee of Environmental Engineering PAS 25.

PN-EN 12390-3:2011 *Testing hardened concrete. Compressive strength of test specimen.*

PN-EN 12457-4:2006 *Characterisation of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction).*

PN-EN 15167-2:2006 *Ground granulated blast furnace slag for use in concrete, mortar and grout. Definitions, specifications and conformity criteria*

PN-EN 197-1:2012 *Cement. Composition, specifications and conformity criteria for common cements*

PN-EN 450-2:2006 *Fly ash for concrete. Conformity evaluation*

Ponikiewski, T.; Gołaszewski, J. (2012). *The high - calcium fly ash as a component of self-compacting concrete.* Eurocoalash 2012 Conference, Thessaloniki, Greece.

Roskovic, R.; Bjegovic, D. (2005). Role of mineral additions in reducing CO_2 emission. *Cement and Concrete Research* 35: 974-978

Regulation of the Minister of Economy of 8 January 2013 on the criteria and procedures for the acceptance of waste for disposal at a landfill. Dz. U. poz. 38.

Song, F.; Gu, L.; Zhu, N.; Yuan, H.; (2013). Leaching behavior of heavy metals from sewage sludge solidified by cement-based binders. *Chemosphere* 92: 344-350

Wzorek, M.; Król, A. (2009). Analysis of selected properties of sewage sludge within the consideration of its energetic application in forming alternative fuels. *Series of Monographs Polish Journal of Environmental Studies* 6: 132-136

Wzorek, M.; Król, A. (2012). Ocena jakości paliw z odpadów stosowanych w procesach współspalania z węglem (Evaluation of the quality of fuels from waste used in co-combustion with coal). *Prace Instytutu Ceramiki i Materiałów Budowlanych* 10: 444-465.

ANNA KRÓL

Rola granulowanych żużli wielkopiecowych w zrównoważonej produkcji cementu oraz gospodarce odpadami

Streszczenie

Zrównoważony rozwój to wezwanie do zachowań innowacyjnych choć ostrożnych, w celu pogodzenia kluczowych obszarów dla ludzkości: rozwoju ekologicznego, gospodarczego i społecznego. Zgodnie z ideą zrównoważonego rozwoju jest wykorzystanie produktów ubocznych z innych branż do produkcji klinkieru, cementu i betonu. Produkty te mogą z powodzeniem zastąpić naturalne minerały lub klinkier w produkcji cementu. To znacząco zmniejsza wydobycie zasobów naturalnych i zwiększa ekonomikę procesu, bez pogorszenia jakości produktu. W technologii produkcji cementu coraz ważniejsza jest rola aktywnych dodatków mineralnych. W procesie produkcji cementu na świecie ma podstawy ekonomiczne, ekologiczne, ale i technologiczne. Celem użycia dodatków jest w istocie produkcja takich cementów, których właściwości pozwolą uzyskać beton o wysokiej wytrzymałości. Znanym dodatkiem mineralnym jest granulowany żużel wielkopiecowy czyli odpad pochodzący z hutnictwa. Ten materiał jest coraz częściej stosowany także w procesie stabilizacji odpadów niebezpiecznych. Zastosowanie żużla granulowanego w przemyśle cementowym oraz w procesie zestalania osadów galwanicznych przedstawiono w pracy wraz z prezentacją własnych badań prowadzonych przez autora w tej dziedzinie.

Słowa kluczowe: granulowany żużel wielkopiecowy, gospodarka odpadami, produkcja cementu, zestalanie, metale ciężkie