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The role of the silica fly ash in sustainable waste management

Anna Król[1,a]

[1]*Opole University of Technology, Department of Environmental Engineering, 5 Mikołajczyka Street, 45-271 Opole, Poland*

Abstract. Mineral construction materials play an important role in waste management. They are often used for solidification of hazardous mineral waste.These processes involve common cement or binders that apart from cement contain other mineral additive, which indeed are post-process by-products from other industries. Among approved mineral additives there is silica fly ash from hard coal combustion in conventional power plants. Such fly ash used during solidification allow formation of stable and durable matrices of high immobilisation potential for heavy metals.The paper presents analysis of effect of addition of fly ash on solidification process of galvanic sewage sludge in comparison to matrices prepared using Portland cement.

1 Introduction

The concept of sustainable development is an assumption of continuous economic and social growth in harmony with the natural environment. This is a pursuit of such an economic model that would provide progress of mankind without destroying supporting it natural systems. This means using natural resources, while respecting them. A sustainable development is not contrary to the progress, but rather a call for keeping equilibrium and moderation in order to reconcile key areas for mankind: ecology, economy and society [1].

Also application of by-products from other industries in production of clinker, cement or concrete is in line with the sustainable development concept. These products can be successfully replaced with natural minerals or clinker in cement production. This way it is possible to significantly reduce output of natural raw materials and improves profitability of the process, without compromising the quality [1].

Also utilization of alternative fuels in the production of Portland cement is consistent with the sustainable development concept. The most of waste with proper minimum energy value can be used for production of alternative fuels. The use of alternative fuels in cement industry has positive impact on clinker production economics and improves environmental effects of fuel combustion (such as reduction in atmospheric emissions of gases and dust). Cement kilns are one of the few plants that use waste-based fuels as a component of conventional fuel. Combustion of alternative fuels combined with fossil fuels is both effective and environmentally safe solution that form a part of energy waste recovery [1-3]. The consumption of alternative fuels in the cement industry in Poland in 2012 was 1180.5 thousands Mg.

Moreover, replacing clinker with other active mineral additives starts to play more and more important role in cement production. In the global cement production, this process is justified by both economy and environment protection, but also by technological reasons. There is a tendency to obtain cements of such properties that would allow obtaining durable concrete, and the application of proper mineral additives can help in that [4].

Cement mineral additives are mainly combustion by-products from power industry and waste generated by iron and steel industry, i.e. silica fly ash (denoted in cement name as V) and granulated blast-furnace slag (denoted as S) [5-7]. Such materials exhibit high pozzolanic and/or hydraulic activity. An important position in mineral cement additives is gypsum used in amount of 4 to 6% cement weight as a binding time regulator. For that purpose mainly gypsum from flue desulfurization of power boilers are used (often called reagypsum).
In the recent years, the interests of cement industry involved also lime fly ash (W) from lignite combustion [8].

According to the data of the Polish Cement Association [9] in 2012, the Polish cement industry consumed over 4,200 thousand Mg secondary raw materials for cement, including over 1,800 thousand Mg of fly ash.

This shows that activity of the cement industry is associated with some environmental benefits. Production of clinker and cement often involves use of by-products from other industries, which helps to remove waste from the environment, while saving reserves of resources or fossil fuels.

Additionally, technology development leads to use of mineral binders for neutralization of hazardous waste in a solidification/stabilization process (s/s). This method

[a] Corresponding author: a.krol@po.opole.pl

has been developed in the mid-20th century for neutralization of radioactive waste. In time, it has been adapted for utilization of other waste, especially of industrial and hazardous, as well as sludge. Waste solidification process allows to modify waste physical and chemical properties, as well as reduce solubility and leaching of hazardous compounds [10,11]. Common cements (compliant with standard [6] requirements in mortars and concretes), and mineral binders of different composition based in particular on mineral additives, are used in order to permanently solidify waste.

The paper focuses on use of silica fly ash in production of binders allowing successful solidification of hazardous industrial waste.

2 Role of silica fly ash in production of mineral binders

Silica fly ash from coal combustion in power industry are relatively well recognized combustion by-products. They are widely used in cement and concrete processing as [8]:
- mineral additives for production of different cement grades (e.g. CEM II, CEM IV/A,B, CEM V/A,B),
- active mineral additive and micro-aggregate for normal and self-compacting concrete,
- one of components for production of high performance concrete,
- component of cellular and road concrete.

Silica fly ash is a material obtained by electrostatic or mechanical precipitation of dust particles from flue gases from conventional furnaces fired with coal dust at temp. approx. +1450^{0}C. Their chemical composition is usually similar to composition of roasted carboniferous slate, which is a main incombustible component of coal. The main components of discussed ash are SiO_2 and Al_2O_3, CaO, SO_3, MgO, Na_2O and K_2O from the degradation of silty materials, pyrite and calcite. A component mainly determining properties of pozzolanic fly ash is unstable silica-aluminum-potassium glass produced as a result of separation of inorganic matter during coal combustion and its subsequent melt and solidification in form of fine, spherical particles (Fig. 1) [8]. Crystalline phases that occur most often in fly ash from coal are quartz and mullite, as well as haemetite and magnetite [8].

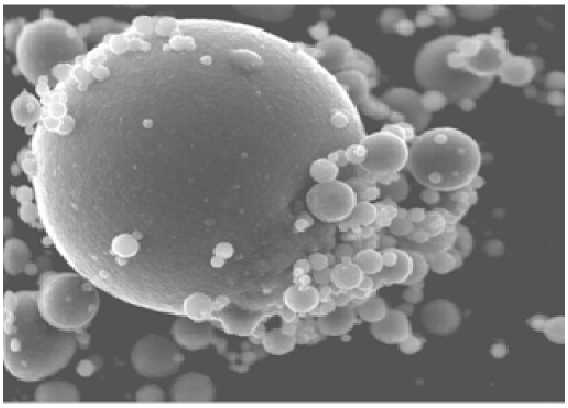

Figure 1. Silica fly ash grains (magnification x 10 000).

A beneficial impact of fly ash on mineral composites consists mainly of [12]:
- increasing grout tightness, due to change of microstructure of set binder matrices,
- formation of additional hydration products, i.e. hydrated calcium silicates (C-S-H phase) and hydrate calcium aluminates filling the pores,
- sealing structures by not hydrated fly ash particles,
- advantageous strength levels in long-term ageing of materials with addition of fly ash.

The listed effects on one hand result from ash acting as aggregate that tightens the grout structure, and on the other hand are related to pozzolate reaction of ash in the grout. Pozzolate reaction is related to formation of additional amount of hydrated calcium silicates that seal grout pores. Comparison of total porosity of ash cement grout with Portland cement grout shows that they are similar, but pore size is smaller in ash cement grout. This is due to the fact that incorporation of fly ash to the grout causes formation of larger amount of gel pores and filling capillary pores with new hydration products. This in turn, reduces permeability which hinders migration of liquid containing among other heavy metals [13, 14]. This also confirms positive effect of silica fly ash on binding heavy metals.

3 Advantages of fly ash application for solidification of hazardous waste

Taking into the account the fact that the aforementioned advantages of silica fly ash regarding formation of permanent structures of mineral composites, it may be said that this is a material applicable for production of matrices for solidification of hazardous industrial waste. Solidification with cement materials allows modification of waste physical properties. This way waste material of reduced (usually low) liquid phase content that is mainly responsible for transport of environmentally hazardous substances.

Waste solidification effectiveness in cement matrix is characterized by two properties: matrix durability and heavy metal leaching [15 - 17]. Unfortunately, these two properties are characterised through many others parameters, which makes unambiguous assessment of composite very difficult. Indeed, only matrix durability depends on its: strength, absorbability, water permeation depth, porosity. And as we know, concretes used for solidification of hazardous waste stored in natural environment or used as aggregate or granulated product in engineering construction can be exposed to many different, unfavourable environmental conditions [18].

The reason for using fly ash from power industry for production of composites solidifying hazardous waste is obtaining matrices of increased durability. Such ash is also to support immobilization of heavy metals in the composite.

4 Material and methods

The conducted tests involved design and preparation of concretes using the following cements:
- Portland cement CEM I 32.5R (denoted hereinafter CEM I);
- Fly Ash Portland cement CEM II/B-V 32.5 R-HSR, in which silica fly ash content was approx. 30% (denoted hereinafter CEM II/B-V).

Contents of heavy metals in cements and in the fly ash used in the studies are presented in Table 1.

A composition of concrete mix was the following: 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 (w/c) ratio in all mixes was equal to 0.6. The mixes prepared in such a manner was used as reference samples. Moreover, samples were prepared with 10% of cement replaced with hazardous waste (GO) – galvanic sewage sludge. Contents of heavy metals in waste is presented in Table 2.

Obtained concrete mixes were formed into cubes of dimensions 10x10x10 cm. After 24h, the cubes were subjected to leaching tests or physicochemical tests. Water extracts from concrete samples or waste samples were produced acc. to PN-EN 12457-4 [19]. According to the procedure described therein, the particulate material to grain size < 10 mm, undergoes shaking with water for 24 hours, while keeping liquid solid (L/S) ratio equal to 10. Heavy metal content in eluates was determined using atom absorption spectrometry.

Pore size distribution was measured using mercury porosimeter PoreMaster 60. The measurements were conducted in range 3.5 nm to 10 micrometers.

Compressive strength of concrete was determined according to the standard PN-EN 12390-3 [20].

Table 1. Content of selected heavy metals in cement and fly ash.

Heavy metal	Content [mg/kg]		
	CEM I	CEM II/B-V	Fly ash
Cr	54	52	97
Zn	316	262	142
Cd	< 1	< 1	11
Pb	24	31	34
Co	7	11	32
Ni	18	26	41
Mn	288	323	482
V	34	63	176
Cu	60	54	71
As	6	11	140
Hg	< 0.08	< 0.08	7
Tl	< 5	<5	160

5 Results

The waste selected for tests cannot be classified as neutral waste. In eluates, significant exceeding of content of heavy metals such as chrome, nickel and cadmium (Table 3) was observed in comparison to allowable metal concentrations in water extracts from waste stored on neutral waste landfills [21].

Table 2. Content of heavy metals in dry matter 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

Hazardous waste often before their disposal undergo solidification. This allows to reduce heavy metal leaching to water or soil.The results obtained for immobilisation of heavy metals from galvanic sewage sludge in matrices made of Portland cement and cement with fly ash addition were determined in two test environments. Some samples were exposed for one year to natural environment, while others were in constant contact with distilled water for the same period

Table 3. Content of heavy metals in water extract from galvanic sewage sludge (GO)

Heavy metal	Concentration in water extract [mg/kg]	Allowable value acc. to [21] for waste water extracts [mg/kg]	
		neutral waste	non-hazardous and non-neutral 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	-	-

Table 4. Leaching of selected heavy metals from hazardous waste (GO) solidifying concrete.

Concrete sample exposure conditions*	**Sample designation**	**Heavy metal content [mg/dm³] in water eluate**					
		Cr	**Zn**	**Ni**	**Cu**	**Cd**	**Pb**
Distilled water	CEM I+GO	0.054	0.021	0.002	0.020	0.0001	0.005
	CEM II/B-V+GO	0.098	0.101	0.004	0.069	0.0001	0.023
Natural environment	CEM I+GO	0.186	0.001	0.020	0.006	0.001	0.044
	CEM II/B-V+GO	0.500	0.001	0.013	0.007	<0.001	0.041

*Samples were exposed for a year at various test conditions.

The obtained concentration of selected heavy metals are presented in Table 4.
The measured leaching is low, while the used concrete mixes allow to significantly reduce leachability of heavy metals. It shall be noted that fly ash Portland cement in comparison with Portland cement increases immobilisation degree of heavy metals (e.g. Ni, Cd, Pb, when matrices are exposed to natural environment).

Decreasing heavy metal leachability may be a result of changes occurring at the level of grout microstructure. Addition of fly ash increases total porosity of samples prepared from CEM II/B-V compared to CEM I, however it also allows reduction of pore sizes. Reduction of average pore size occurs also with the addition of only waste to the concrete mix. Pore size decreases also with time. This is a result of pores being filled with subsequent hydration products. Distribution medians presented in Table 5 indicate that average pore size in the tested grout
is in the range corresponding to gel pores, which is important in terms of heavy metal leaching. Gel pores are closed pores, which inhibits liquid transport outside the matrix. The tests results on matrix porosity are presented in Table 5.

The matrices used for neutralization of hazardous waste must have high durability under conditions of the During the studies, concrete samples with addition of by natural environment. This property is determined mainly compressive strength of such composites hazardous waste were measured for their strength. The tests were conducted both for samples stored in distilled water, and for samples exposed to atmospheric environment for one year.

The strength test results presented in Table 6 show that cement with addition of fly ash (CEM II/B-V) not only maintains similar strength as Portland cement when the samples are exposed to natural environment, but when samples are constantly exposed to water for one year, it shows greater strength. This shows high durability potential of such matrices and obtaining better dependability of solidification process stability under various exposure conditions.

6 Conclusions

Hazardous waste management poses a challenge for all communities, thus becoming a very important element of global system for environmental care. The system requires that used methods and processes are in line with foundations of the sustainable development. Therefore, waste management shall be conducted in such a manner to protect natural environment, and if possible, use also

Table 5. Open porosity (P) and pore size distribution in grout with and without hazardous waste (GO), after 1 and 6 months of hydration.

Hydration period	**Grout using:**	**P [%]**	**Median value [μm]**	**Modal values**
1 month	CEM I	10.32	0.105	0.20 – 0.01 – 0.006 -<0.004
	CEM II/B-V	11.24	0.074	0.26 - 0.013 - 0.01 - 0.004
	CEM I+GO	13.61	0.072	0.55 - 0.05 - 0.01 - 0.004
	CEM II/B-V+GO	15.46	0.055	0.52 – 0.05 – 0.01 -<0.005
6 months	CEM I	14.61	0.094	0.52 - 0.09 - 0.02
	CEM II/B-V	15.86	0.057	0.54 - 0.06 - 0.006
	CEM I+GO	20.47	0.048	0.54 -0.015
	CEM II/B-V+GO	24.45	0.042	0.58 – 0.04

Table 6. Compressive strength of samples stored for one year under different conditions.

Concrete designation	Storage conditions	Compressive strength [MPa]
CEM I+GO	Natural environment	40.3
	Distilled water	40.6
CEMII/B-V+GO	Natural environment	38.3
	Distilled water	50.4

Waste disposal method that is solidification/stabilisation may be one such example. For neutralization of hazardous waste common cements are used, but also combustion by-products such as silica fly ash from coal combustion in the power industry.

Use of fly ash may result in reduction of consumption of cements, which production is expensive and energy-consuming.

Study results presented in the paper show that use of fly ash in solidification of galvanising sludge is a correct, or even a desired, action. This way matrices of increased content of gel pores are obtained, where release of pore liquid to the natural environment is reduced. Thus reducing transport of liquid containing heavy metals from wastes. This leads to increasing immobilization degree of heavy metals in solidifying composites containing fly ash. Additional advantage is increase in strength of matrices containing fly ash in comparison to Portland cement-based matrices (CEM I).

Hence, fly ash gives hope and opportunity to conduct waste solidification process in a stable manner while observing environmental protection principles. The application of silica fly ash in this process is therefore in line with the concept of sustainable waste management.

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