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Ecological and Economic Savings of Fly Ash Using as Geopolymer

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1. Introduction

Geopolymer are rather new and not so known alternative materials. Number of geopolymer is replacing naturally appearing materials due to their unique characteristics. Therefore society should to give attention to by-products or waste, such as geopolymer from fly ash that could be contribution from ecological, as well as from economic aspect. Every year European Union produces several hundred millions of fly ash as a waste from heat and energy production. There are different types of industrial wastes such as biomass ash, red mud, recycled glass and heavy metals waste, in their application for geopolymer production (Toniolo & Boccaccini 2017).

Fly ash belongs to the group of by-product from coal burning, stocking to the pond, where its specific physical and chemical characteristics are degraded. According researches fly ash could be full valued raw material, replacing some naturally appearing materials, or in dependence of qualitative characteristics of the coal it could be more convenient than naturally appearing materials. Common use of fly ash using is filling of not used mining spaces, application to the soil, in which fly ash improves significantly its physical, chemical and mechanical characteristics.

Number of professional, scientific research papers published on geopolymer was close to zero in 1991, it rose to over 400 per year in 2013 (Geiger 2011). Abroad, fly ash as a raw material is used for decades, since it presents cheap raw material, often with sufficient functional characteristics, usually without harmful effects on humans or the environment (Rosik-Dulewska & Karwaczyńska 2008, Davidovits 2011). But not many laics have idea about their existence and possibilities for using in the industry and living environment protection. Geopolymer had become common idea mostly in USA, in France and India, where there is given great attention during whole decades (Vilamová & Piecha 2016). In addition to various technical and technological aspects of fly ash using, which favorably affects the characteristics of the materials, their use also has substantial economic and environmental benefits (Ahmaruzzan 2010). Fly ash with a high content of residual coal can also serve to remove various inorganic substances (Iyer & Scott 2001). Moreover, recent studies have shown that geopolymer concrete based on fly ash does not require such heat treatment, when there is not added a small volume of the ingredient, which is a carrier of calcium, for example a slag (Yao 2015). The experimental investigations on the compressive strength and permeation properties of geopolymer concrete prepared with low calcium fly ash (Jindal et al. 2017).

Using of geopolymer in agriculture had been studied by (Suksiripattanapong et al. 2017) that investigated the strength and microstructure properties of spent coffee grounds (CG) stabilized with rice husk ash (RHA) and slag geopolymers to produce a green construction subgrade material (Suksiripattanapong et al. 2018). The outcome of this research will enable CG, furnace slag and RHA waste products to be used as sustainable materials in pavement applications. The amount of sludge wastes produced from mining, domestic agriculture and industrial activities are about 60200 tons per year. The waste increase will have a significant impact on the energy conservation and also on the environment. Geopolymer has an ability to encapsulate heavy metals. In this sense Abdullah et al. (2016) studied the potential of sludge waste to be utilized as construction materials, finding its effective using in the area (Abdullah et al. 2016). Other possible geopolymer using can be as boiler ash waste from waste of palm oil industry, which provide area of potential use as raw material for geopolymer production (Yahya et al. 2013).

As a result of across the world, water is contaminated with nutrients and pesticides which threaten riverine environments, wetlands, urban drinking water supplies and also marine assets. Much can be done and sustainable management practices (SMP) can be put into place to reduce water impacts from agriculture. Required investment levels are insignificant compared to the economic advantages to be gained from adopting appropriate SMP across global agribusiness. SMP technologies need to be targeted at specific pesticides (eg. atrazine, simazine, diruron, ametryn, hexazinone, tebuthiuron, dieldrin, metalochlor, 2,4 D, triclopyr, picloram and bromacil). Research, development and testing of appropriate non-leaking/reactive spillways and subsurface of geo structures need to take place across the various agricultural industries. The challenge for engineers is to come up with geo structural designs which are efficient, cost effective and which will be taken up and embraced by Australian and world agribusiness (Craig et al. 2015).

The other research of fly ash using in concrete production studied the interface between fly ash concrete and steel rebar (Liang et al. 2017). The results showed that the general shape of the bond-slip curve between fly ash concrete and steel rebar was similar to that for the normal concrete and steel rebar.

2. Experimental

The main target of the research was to compare economic and environmental contribution of fly ash. Comparison had been done in case of concrete production with and without fly ash using.

Object of searching is fly ash, rising during coal burning in heat and electric energy production, which is possible without further elaboration to use as an input raw material in the industry, especially during concrete prefabricates production:

a) as a full replacement or

b) as partial replacement of cement in final concrete mixture for prefabricates production.

The process of searching for fly ash using and its contributions was according calculation of costs for production of concrete with and without fly ash using. Data had been obtained from price list of individual materials for concrete production as follows:

1. Data collection: type of materials used, unit prices per materials.
2. Calculation of assumed consumption of individual types of material.
3. Total costs calculation for individual types of concrete.
4. Comparing of costs effectiveness with determination of benefit of fly ash using.

5. Determination of resulting values of alternatives (with or without fly ash).
6. Decision, which alternative is convenient.

The cost calculation for the concrete production with using of geopolymer is based on the properties of individual types of concrete, which provide technical standards, as well as the requirements of the individual components. Concretes are divided into 16 basic strength classes under current Slovak technical standard norm EN 206-1. National Annex to this standard provides requirements and specifications for all types of concrete, as well as the conditions, under which the concrete can be used. All mentioned characteristics are included in calculation according Table 1.

Table 1. The cost calculation for the concrete production with using of geopolymer
Tabela 1. Kalkulacja kosztów produkcji betonu z użyciem geopolimerów

	Total price [€]	Volume of concrete prefabricate [m^3]	Price of concrete prefabricate [€]	Possible fly ash consumption [t]	Possible price savings [€]
1st section					
2nd section					
.....					
n - section					
total					

Cement is the most active part of the concrete and it is usually the most expensive. Its selection and proper using is essential to achieve economic balance between the desired properties of the prepared concrete mix and the cost of its production. We calculated with cement category I and II, since it is the most popular among manufacturers of concrete, ensuring an adequate level of strength and durability.

3. Results and discussion

Geopolymer as a new material is used for surface treatment and bonding, binders for fiber composites, encapsulation of waste as well as cement for concrete production. Using of geopolymer is searched in number of scientific and industrial sectors: modern inorganics chemistry, physical chemistry, colloidal chemistry, mineralogy, geology and all types of technological processes. Broad scale of potential application includes: resistant materials, decorative artefacts from stone, heat isolation, technologically not demanded construction materials, energetically not demanded ceramic pavement, fireproof elements, biotechnology (material for medicine using), foundry industry, cement and concrete, elements for infrastructural repairs and reinforcement, technological elements for aerial and automotive industry, resinous systems, packages for radioactive and toxic waste, arts and decoration, archeology, etc. (Davidovits 2011) . Main using in the individual sectors is given by Table 2.

Table 2. Possibilities for fly ash using as raw material in various sectors
Tabela 2. Możliwość wykorzystania popiołów lotnych jako surowca w różnych sektorach

Sector	Possibilities for using
Metallurgy	Steel production, preparation of heating layers, preparation of backfills, forming mass during casting steel
Mining	Establishment of mined mining spaces
Agriculture	Treatment of heavy soils, preparation of bio organic material fertilizers, seed dressing as a source of micro and macro elements
Construction	Production of artificial stones and concrete, production of ceramics and bricks, road construction

The fly ash contains significant amounts of SiO_2, Al_2O_3, CaO and Fe_2O_3, which are considered low-cost materials for the ceramics industry. In addition, the powdery consistency makes the ash a suitable material that can be mixed into ceramics adhesives and adhesives without any treatment. As for the using of kaolin clay and fly ash in the manufacture of ceramic tiles and floor tiles for interiors and exteriors, the results of research have been so good that they have achieved the quality of commercial ceramic materials. In addition, glass ceramic and ceramic materials from fly ash without further additives have achieved better physical, chemical and mechanical properties (Yao 2015).

Metals and metal oxides are often used as catalysts in various industrial applications. Fly ash is composed of various oxides of metals with high ferric oxide content and achieves high thermal stability. Chakraborty and his team prepared CaO catalyzed with fly ash support for transesterification of soybean oil and showed a high catalytic efficiency in converting soybean oil to biodiesel with a high fatty acid content of up to 96.97% (Yao 2015).

3.1. Fly ash as a waste

Coal using is inseparable part of human activity. In past time coal played very important role and it is still remaining, either for electric energy production, or steel production, or as a source of heat. Only in EU countries consumption in 2012 was 837 million tons of coal, in the world it presented 6,6 billion tons of coal (see Table 3) (International… 2017).

Table 3. Annual coal consumption in tones
Tabela 3. Roczne zużycie węgla w tonach

	2009	2010	2011	2012	Average / year
Slovakia	8 567 164	8 415 045	8 288 279	7 691 523	8 240 503
EU-27	776 680 000	786 142 000	812 833 000	837 620 000	803 318 750
Europe	959 656 000	966 325 000	1 003 697 000	1 026 713 000	989 095 250
World	7 471 823 000	7 750 518 000	8 123 601 000	8 449 496 000	7 948 859 500
Growth (t)		278 695 000	373 083 000	325 895 000	
Growth (%)		3,73	4,81	4,01	

According statistics coal consumption in the world is increasing more than 4% per year, as well as volume of fly ash. Whole world annual increase is 550 million tons of fly ash and only 30% of total volume is produced in Europe and it is used as secondary raw material. 70% presents not used waste (Špak et al. 2012). Also improper treatment with fly ash became environmental problem. In present time there is pressure to the research in area of fly ash recycling. Important task in consequent treatment with fly ash or its using plays physical, chemical and mineral characteristics of individual fly ashes. Specific characteristics depend on coal type, conditions of burning, setting the collection device.

3.2. Influence of Portland concrete production to the living environment

Broad using of fly ash is production of Portland concrete, but during its production there is greenhouse gas emission to the atmosphere. During clinker production there is produced 0,55 tons of chemical CO_2 and its production demands burning of carbon fuels, which increases the number by other 0,44 tons. Exception is mixed concretes with fly ash, due to which CO_2 emission is decreased by 10-15% (Antošová et al. 2013). Mentioned is illustrated in Table 4, 5.

Table 4. Comparing of emission during production of Portland and geopolymer concrete
Tabela 4. Porównanie emisji w trakcie produkcji cementu portlandzkiego i geopolimerowego

CO_2 emission (t)	Burning	Crushing	Solvents	Total	Reduction
Portland Concrete	1,000	0,020	0	1,020	0
Geopolymer Concrete	0,140	0,018	0,050	0,208	80%

Table 5. Comparing of energy consumption during production of Portland and Geopolymer Concrete
Tabela 5. Porównanie zużycia energii do produkcji cementu portlandzkiego i geopolimerowego

Energy consumption (MJ/t)	Burning	Crushing	Solvents	Total	Reduction
Portland Concrete	4 270	430	0	4 700	0
Geopolymer Concrete	1 200	390	375	1 965	59%

3.3. Fly ash as a secondary raw material using

In present time almost everybody perceives necessity to use secondary raw materials. This trend is obvious in the industry, where using of secondary raw materials can increase economic effectiveness of the production. Considerable is also contribution of secondary raw materials using in area of living environment protection, since it backwardly uses wastes from industrial activity (Sisol et al. 2014). Comparing of production and using of secondary products from coal burning in USA and EU is given by Table 6 and 7.

Table 6. Production and using of secondary products from coal burning in USA in 2013
Tabela 6. Produkcja i zużycie odpadów ze spalania węgla w USA w roku 2013

	Fly ash	Ash	Slag
Produced volume	53 400 000	14 450 000	1 355 939
Consumed volume (t)	23 321 230	5 640 693	897 185
Consumed volume (%)	43,67	39,02	66,16
Concrete /concrete products	12 356 726	497 074	0
Mixed concrete / clinker additive	2 286 144	1 324 131	0
Construction fillings	3 141 454	2 140 800	0
Agriculture / soil treatment	284 106	457 287	1 000
Using during snowing	0	421 087	11 797
Using in mining	1 843 292	250 113	0
Waste stabilization	2 034 182	59 751	727
Services for oil fields	313 373	73 883	0
Others	1 061 953	319 567	895 542

Table 7. Production and using of secondary products from coal burning in EU 15 in 2010
Tabela 7. Produkcja i zużycie odpadów ze spalania węgla w 15 krajach Unii w roku 2010

	Fly ash	Ash	Slag
Produced volume	31 616 000	4 052 000	1 000 000
Consumed volume (t)	13 785 000	1 890 000	1 000 000
Consumed volume (%)	43,6	46,64	100,00
Concrete production	2 152 000	178 000	0
Mixed concrete	1 947 000	1 000	0
Concrete additives	4 947 000	62 000	3 000
Concrete blocks	760 000	798 000	0
Ceramics / bricks	83 000	16 000	0
Fillings	3 174 000	513 000	0
Soil treatment	115 000	0	0
Temporary storages	201 000	87 000	0
Storage at landfill	2 260 000	87 000	0
Others	607 000	322 000	997 000

3.4. Economic aspects of fly ash using

Using of geopolymer in the industry offers some economic benefit, since costs for fly ash are negligible. Producers of heat and electric energy treat fly ash as a waste, which presents for them a problem. Waste stocking has its limitation, legislative as well as its localization and capacity (Okoro et al. 2017).

For example in Slovakia according Statistical Office in 2013 there was produced 286 863 663 kg of concrete prefabricates, which presents 120 000 m^3 concrete, necessary for its production. In case producers would replace Portland concrete with concrete, mixed with fly ash, 9 360 tons of fly ash could be consumed (Khouri et al. 2016).

Economic contribution of fly ash using will be illustrated by case of National Highway Society, Joint Stock Company, supplying concrete prefabricates in volume 14 678 m^3. During production of such prefabricates part of concrete could be replaced with fly ash, which could mean economic evaluation by almost 1 150 tons of fly ash and saving more than half a million euro. Table 8 concludes all possible economic savings.

Table 8. Possible fly ash using and savings for highway construction
Tabela 8. Możliwości wykorzystania popiołów lotnych przy budowie autostrad i uzyskiwane oszczędności

	Total price [€]	Volume of concrete prefabricate [m^3]	Price of concrete prefabricate [€]	Possible fly ash consumption [t]	Possible price savings [€]
D1 Trnava – crossing Lúka	9 399 451	7 501	1 289 546	586	232 118
D1 Ivachnová – Važec	32 628 700	5 288	1 262 959	413	227 332
D1 Prešov – Budimír	14 998 877	1 889	306 332	148	55 139
Total	57 027 028	14 678	2 858 837	1 145	514 589

In case Slovak Republic would install condition for fly ash using as partial replacement of cement for concrete prefabricates, used during highway construction, till 2020 volume of fly ash could decrease by more than 11 000 tons. Savings in individual years are calculated according Table 9.

Table 9. Plan of highway construction in Slovakia during 2015-2020
Tabela 9. Plany budowy autostrad w Słowacji w latach 2015-2020

Year	Planed road construction [m]	Assumed volume of necessary prefabricates [m^3]	Estimated volume of fly ash, necessary for prefabricates production [t]
2015	71 274 m	9 266 m^3	723 t
2016	175 240	22 782	1 777 t
2017	148 580	19 316	1 507 t
2018	45 510	5 917	462 t
2019	60 850	7 911	618 t
2020	606 400	78 832	6 149 t
Total	1 107 854	144 024	11 236 t

According available literature there was no suggested such structure of concrete mixture, which could content higher rate of fly ash, achieving at least 50 MPa resistances. While using of concrete with 30 MPa resistances in concrete prefabricates, it could mean replacing yet 30% cement with fly ash and in this case resulting price would be lower, since volume of cement, necessary for production would decrease and at the same time waste material would be consumed.

4. Conclusions

Although fly ash cannot be put into practice economically, the CO_2 production of Portland cement remains an open problem as well as the way the fly ash treatment. It is only a matter of time when it will be necessary to take much stricter measures to reduce emissions so that global warming and the associated global dimming are at least slowed down as it is not possible to stop it completely. It is undeniable that the industry will still need concrete, so the demand for Portland cement will not fall naturally.

Concrete with fly ash is an alternative that would replace Portland cement, but only if the cost of water glass is reduced to a level comparable to the price for Portland cement, and if it is questionable whether construction engineers are going after a not yet well-known alternative, or if they even at the cost of higher costs continue to prefer a traditional, verified option.

One of the possibilities that could help to solve problem with high CO_2 production, which is costly affordable, is the use of biomass in cement production, with aim to at least partially reduce emissions that are released into the atmosphere. Another possibility is the recycling of old concrete, which by its properties can replace part of aggregate in new concrete, or it can be used as a foundation for road construction. Similarly fly ash could be used as a mixture to concrete.

In spite of mentioned aspects fly ashes produced in eastern Slovakia, having a high content of unburned coal residues (more than 10% LOI), cannot be utilized as a secondary raw material for building materials. Currently, one possibility for the utilization of high-LOI (Loss On Ignition) fly ashes is in the synthesis of geopolymers (Geopolymer... 2015). Also there is necessary to deal with ash, since due to industrialization, several countries have attained sustainable development with some degree of environmental degradation. These activities influence the environment; however tend to produce pollutants (gases, acids, oils, cooling water, ash and so on) (Okoro et al. 2017). Re-use of fly ash presents system approach as a potential tool to support further regional development, but only during accepting of valid legal regulations of the country, as well as the principles of sustainable environmental development (Khouri et al. 2016).

Awareness of the society has so far insufficiently focused on the possibilities offered; recycling is a business issue for PR, which is presented to the public. According to the European Commission's statistical indicators, only one-third of the produced construction waste is reused, and the reason for such a small amount is not technical problems, but the traditionally used methods in the industry. Netherlands presents a leader in recycling of waste, which yet 95% waste, rising in the industry, is reused. Average of EU member states is against Netherland only 30-60%. It can be not easily predicted, if society will still slather rare sources and alternatively, similar qualitative materials stock at the dump as a waste (Geopolymer... 2015).

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Ekologiczne i ekonomiczne oszczędności wynikające z zastosowania popiołów lotnych jako geopolimeru

Streszczenie

Głównym celem badań było porównanie wpływu popiołów lotnych na gospodarkę i środowisko. Porównanie przeprowadzono dla produkcji betonu z użyciem popiołu lotnego i bez niego. Wyniki pokazują, że popioły lotne mają w pływ na ochronę środowiska i oszczędności podczas produkcji betonu.

Geopolimery to raczej nowe i mało znane materiały alternatywne. Liczne geopolimery zastępują materiały naturalne ze względu na ich unikalne cechy. Dlatego społeczeństwo powinno zwracać uwagę na produkty uboczne lub odpady, takie jak geopolimer z popiołów lotnych, które mogą mieć pozytywny wpływ na środowisko jak i ekonomię. Każdego roku Unia Europejska produkuje kilkaset milionów popiołów lotnych jako odpad z produkcji ciepła i energii. Popiół lotny powstaje podczas spalania węgla i jest składowany na hałdach, gdzie jego szczególne właściwości fizyczne i chemiczne ulegają degradacji. Zgodnie z badaniami popiół lotny mógłby być pełnowartościowym surowcem, zastępując niektóre naturalnie występujące materiały, lub w zależności od cech jakościowych węgla może być wygodniejszy niż materiały naturalne. Powszechne stosowanie popiołów lotnych polega na wypełnianiu wyrobisk górniczych, aplikacji do gleby, w której popiół lotny znacznie poprawia jej właściwości fizyczne, chemiczne i mechaniczne.

Chociaż zastosowanie popiołów lotnych, z punktu widzenia ekonomii, jest niemożliwe, emisja CO_2 z produkcji cementu portlandzkiego pozostaje problemem otwartym, podobnie jak sposób przetwarzania popiołów lotnych. Jest kwestią czasu, kiedy konieczne będzie podjęcie znacznie ostrzejszych środków w celu zmniejszenia emisji, tak aby globalne ocieplenie i związane z nim globalne zaciemnianie uległy przynajmniej spowolnieniu, ponieważ nie można go całkowicie zatrzymać. Nie można zaprzeczyć, że przemysł nadal będzie potrzebował betonu, więc popyt na cement portlandzki nie spadnie naturalnie.

Beton z popiołem lotnym to alternatywa, która zastąpiłaby cement portlandzki, ale tylko wtedy, gdy koszt szkła wodnego obniży się do poziomu porównywalnego z ceną cementu portlandzkiego, a jest wątpliwe, czy inżynierowie budowlani będą stosowali nie do końca jeszcze dobrze znaną alternatywę, nawet pomimo wyższych kosztów niż tradycyjną, zweryfikowaną opcję.

Jedną z możliwości, które mogą pomóc rozwiązać problem związany z wysoką produkcją CO_2, która jest dostępna finansowo, jest wykorzystanie biomasy do produkcji cementu, w celu przynajmniej częściowego zmniejszenia emisji do atmosfery. Inną możliwością jest recykling starego betonu, który dzięki swoim właściwościom, może zastąpić część kruszywa w nowym betonie lub może być wykorzystany jako fundament do budowy dróg. Podobnie popioły lotne mogą być użyte jako składnik betonu.

Abstract

The main target of the research was to compare economic and environmental contribution of fly ash. Comparison had been done in case of concrete production with and without fly ash using. Results speak about contribution of fly ash using in area of living environment protection and costs savings during concrete production.

Geopolymers are rather new and not so known alternative materials. Number of geopolymer is replacing naturally appearing materials due to their unique characteristics. Therefore society should to give attention to by-products or waste, such as geopolymer from fly ash that could be contribution from ecological, as well as from economic aspect. Every year European Union produces several hundred millions of fly ash as a waste from heat and energy production. Fly ash belongs to the group of by-product from coal burning, stocking to the pond, where its specific physical and chemical characteristics are degraded. According researches fly ash could be full valued raw material, replacing some naturally appearing materials, or in dependence of qualitative characteristics of the coal it could be more convenient than naturally appearing materials. Common use of fly ash using is filling of not used mining spaces, application to the

soil, in which fly ash improves significantly its physical, chemical and mechanical characteristics.

Although fly ash cannot be put into practice economically, the CO_2 production of Portland cement remains an open problem as well as the way the fly ash treatment. It is only a matter of time when it will be necessary to take much stricter measures to reduce emissions so that global warming and the associated global dimming are at least slowed down as it is not possible to stop it completely. It is undeniable that the industry will still need concrete, so the demand for Portland cement will not fall naturally.

Concrete with fly ash is an alternative that would replace Portland cement, but only if the cost of water glass is reduced to a level comparable to the price for Portland cement, and if it is questionable whether construction engineers are going after a not yet well-known alternative, or if they even at the cost of higher costs continue to prefer a traditional, verified option.

One of the possibilities that could help to solve problem with high CO_2 production, which is costly affordable, is the use of biomass in cement production, with aim to at least partially reduce emissions that are released into the atmosphere. Another possibility is the recycling of old concrete, which by its properties can replace part of aggregate in new concrete, or it can be used as a foundation for road construction. Similarly fly ash could be used as a mixture to concrete.

Słowa kluczowe:
popioły lotne, geopolimer, ochrona środowiska, oszczędności ekonomiczne, Słowacja

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