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The study of ecological impact of fly ash-based geopolymer binders on soil and aquatic biota

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Abstract. Coal power plants represent the large source of environmental pollution in soils, ground and surface water by leaching out toxic compounds from open landfilled and impounded coal combustion residuals (CCR) such as fly ash. The use of fly ash as a main component in geopolymer binder (GB) systems is one of the effective methods of CCR beneficial utilization. The toxicity assessment as well as leachability of harden geopolymers were tested in aqueous media where oat seeds were used as affected test objects. Bio-resistance of the developed geopolymers was evaluated by the resistance to mold fungi growth. The developed geopolymers demonstrated a very low toxicity and leachability to the biota based on the low effect to germinating ability and growth retardation of the exposed oat seeds. Therefore, the studied fly ash products were proved to be environmentally safe when used in GB systems. The absence of fungi growth observed on the surface of geopolymer samples demonstrates high bio-resistance.

1. Introduction

Enormous amount of unused industrial secondary and by-products pose serious global environmental issues. In this regard, currently a big effort from research institutes is led towards reduction of ecological risk, recycling and beneficial use of the industrial by-products [1-9].

An efficient use of industrial by-products focuses to solve the following problems:

- reduction the amount of industrial wastes released to the environment;
- cleaning up large areas used for landfills and impoundments, and therefore elimination the sources of soil and water contamination;
- beneficial use of industrial hazardous by-products and waste in different applications. Coal combustion residuals considered to be environmentally hazardous contaminants due to elevated amounts of toxic, radioactive components and heavy metals [10, 11].

Based on the research data [12–18], production and application of fly ash-based geopolymers is a very efficient approach to solve ecological issues mentioned above. In addition, due to its structure,

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geopolymers are enabled to encapsulate certain hazardous elements and oxides and, so, preventing their leaching into the environment.

Early study [19] have investigated the influence of low-calcium fly ash products on life activities of flora and fauna. In some cases, [20] it was observed a negative effect to biota due to release of the ions such as Na^+ and Cl^- as well as SO_3 and CaO oxides.

Nevertheless, the use of fly ash as a major component in geopolymer binders assumes an encapsulation and, so, prevention the release of toxic oxides and chemical elements into the environments.

At the same time, the research focused on fungicidal properties of some fly ash products [2, 21–23] experimentally demonstrated no obvious negative effect on mold fungi and, so declaring a safe co-existence of the developed geopolymers with the ecosystem. However, fungi growth can cause a bio-corrosion and durability issues of the developed binders.

This study was focusing on the toxicity of fly ash-based geopolymers by studying the response of vegetation on the example of oat seeds and bio-resistance to mold fungi growth.

2. Materials and Methods

2.1. Materials

Four low-calcium fly ash products from different coal power plants were used in this study to produce geopolymers. Portland cement CEM I 42,5N was used as a reference binder material. Chemical composition of the cementitious components is shown in Table 1.

Aerated distilled water as a reference aqueous media and NaOH with the purity of 98 % as an alkaline activating agent were used for the preparation of geopolymer binder systems.

2.2. Methods

Evaluation of the growth retardation of higher plants was performed using a method of phytotoxicity determination according to Russian Standard GOST 33777-2016 2016 «Surface-active agents. Method for determination of phytotoxicity for higher plant seeds». Bio-resistance of the developed geopolymer binders was evaluated by evaluating resistance to mold fungi growth according to Russian Standard GOST 9.048-89 «Unified system of corrosion and aging protection. Technical items. Methods of laboratory tests for mold resistance».

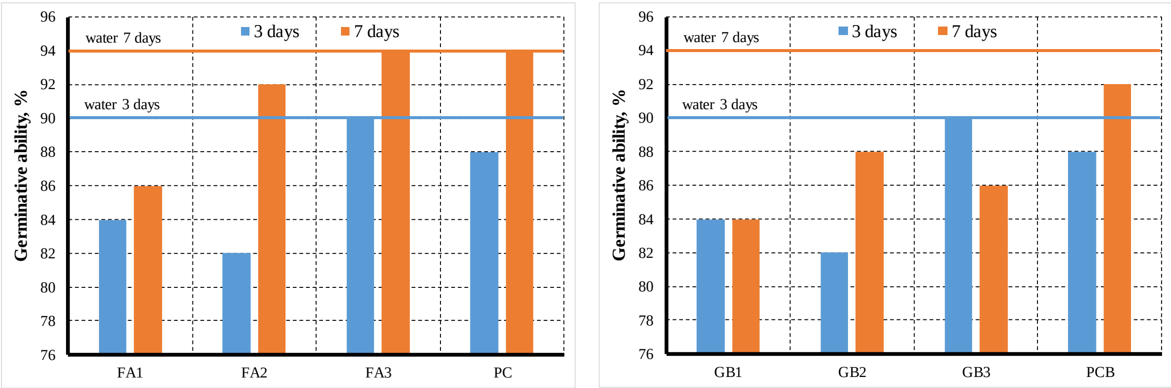
Table 1. Chemical composition of fly ash products and Portland cement.

Material ID	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	TiO_2	ZrO_2	LOI
FA1	59.0	28.3	1.0	4.6	0.1	1.0	3.7	0,6	0.7	0.4	0	0	0	6.1
FA2	60.2	30.9	.	3.4	0.1	0.6	1.3	0,5	0.8	0.5	0	0	0	1.9
FA3	47.3	28.7	1.1	16.2	0	1.0	3.4	0,9	1.7	0.5	0	0	0	1.9
PC	19.1	5.2	0.3	3.6	0	1.3	65.4	0	0.6	0	3.5	0.3	0	0.2

3. Results

3.1. Phytotoxicity

For phytotoxicity evaluation of the fly ashes and the developed binder systems, water extracts of the fly ashes and crashed geopolymer samples at the age of 28 days were taken and then used to prepare water solutions in ratios of 1/10, 1/100 and 1/1000. The prepared solutions were placed to the separate Petri dish covered with filter paper. On top of each Petri dish with filter paper were placed a certain number of oat seeds and stored in a thermostat for 7 days.



a b

Figure 1. Phytotoxicity level of a) cementitious components and b) fly ash-based GBs and PCB based on value of germinative ability.

Visual inspection of the oat roots growth was done after 3 and 7 days of exposure to the aqueous extract of fly ash and fly ash-based geopolymers. The results of the experiment showed that the oat roots exposed to 1/10 extract had about a 35 % decrease in growth rate as shown in Figures 1 and 2. For phytotoxicity evaluation of fly ash products and geopolymer binders average germinative ability (Figure 1), average coat root length (Figure 2) and retardation effect (Figure 3) were used as controlling parameters.

Retardation effect E_r in this study was calculated as a difference between root lengths for oats exposed in reference (L_o) and experimental (L_1) aqueous media using Equation (1):

$$E_r = 100\,(L_o - L_1)\,/\,L_o \tag{1}$$

where E_r is a retardation effect, %;
L_1 is average oat root length in experimental aqueous medium, mm;
L_o is average oat root length in reference aqueous medium, mm.

According to the Guidelines MR 2.1.7.2297-07 «Hazard assessment for production and use of industrial wastes and by-products by the level of phytotoxicity» phytotoxic effect takes place if the E_r is higher than 20 %.

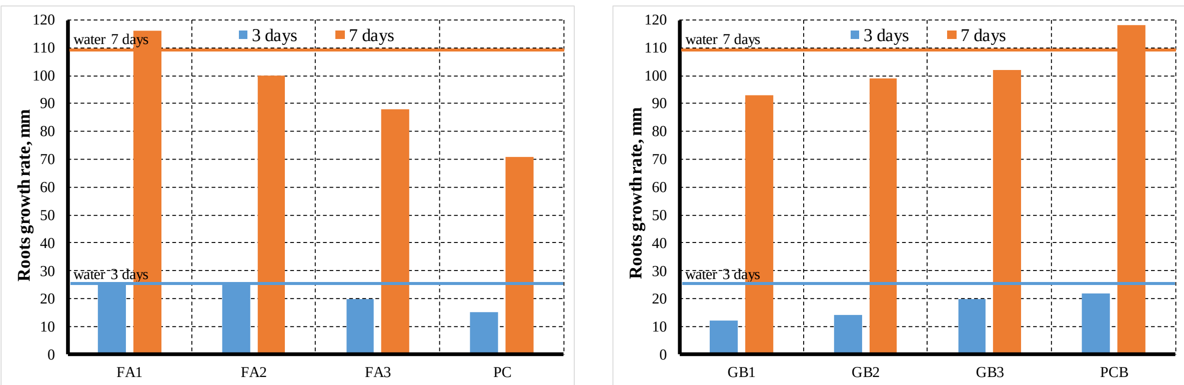


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Figure 2. Phytotoxicity level of a) cementitious components and b) fly ash-based GBs and PCB based on value of roots growth rate.

The oat seeds exposed to more dilute solutions have not displayed apparent acceleration or retardation in roots growth. Based on the phytotoxicity study the fly ash-based binders showed a more apparent retardation effect on oat seeds growth rate than pure fly ash products (Figure 3). The highest degree of retardation was observed for the FA3 and GB3 samples, which is 19.3 % and 6.4 %, respectively (Figure 3, a).

Regarding fly ash products, the lowest or zero retardation effect was observed for the FA1 and FA2 samples. At the same time, PC demonstrated the highest up to 34.9 % of growth retardation. However, the opposite effect was observed for the GB samples (Figure 3, b), although the growth retardation is for the geopolymers considerably lower in comparison with that for the PC sample. Thus, the highest E_r value 14.7 % was detected for GB1 and the lowest E_r of 6.4 % was observed for GB3. In this study, the retardation effect for PCB had a negative value of - 8.2 %.

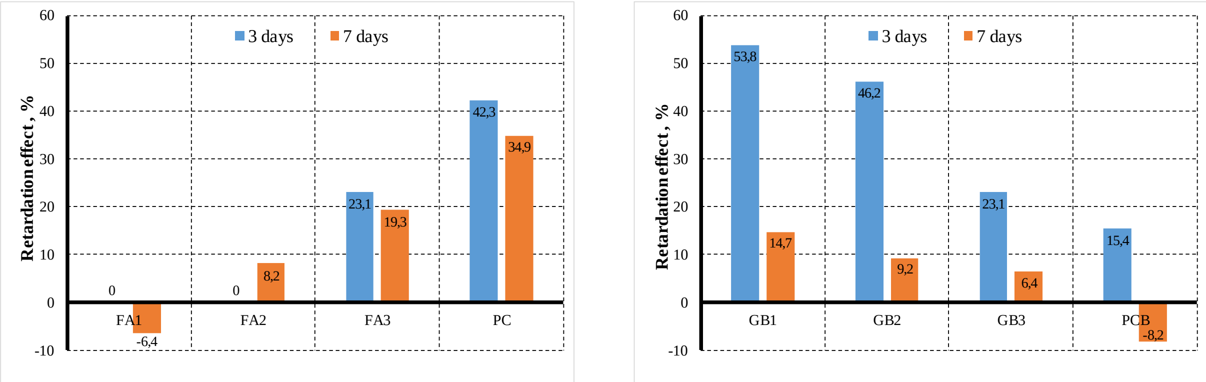

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Figure 3. The retardation effect of fly ash products and PC and the binders on their basis on oat seeds growth rate**.**

3.2. Fungicide resistance

Bio-resistance of the studied cementitious components and developed binders was evaluated through resistance to mold growth according to the Russian Standard GOST 9.048-89 (Table 2). Using standard procedure, the fungicide resistance was evaluated based on the growth index that ranges from 0 to 5. In this experiment, the GB and Portland cement binder (PCB) samples were first saturated with water suspension that contained fungi spores *Aspergillus niger* and then placed in a chamber with 98 % humidity for 28 days.

Table 2. Resistance to mold growth on the surface of low-calcium fly ash products.

Material	Growth index		Fungicide resistance
	Before washing	After washing	
	Cementitious components		
FA1	5	5	Low
FA2	5	4	Low
FA3	5	5	Low
PC	5	0	High (after washing)
	Binder systems		
GB1	5	0	High (after washing)
GB2	0	0	High
GB3	0	1	High
PCB	0	0	High

The samples were then removed from the chamber and evaluated for fungicide resistance using optical microscope Axio Scope Al (Carl Zeiss Jena). A sample was considered highly resistant to fungi growth if the growth index or the population of the mold on the sample surface less than 1. The results of the experiment are presented in Table 2.

The intensive mold growth on the surface of the studied fly ash products (Figure 1 a) indicates the metals and other compounds leaching from CCRs [20] do not have a harmful effect on mold population, and the mineral compounds are suitable for metabolisms of microorganisms.

For fly ash-based geopolymers and PCB samples there is no evidence of mold growth (Figure 4 b), which indicates a high fungicide resistance of the samples. In the Petri dish, there was observed a clearly defined fungicidal zone around binder sample with no sign of mold population. The presence of fungicidal zone (Table 3) in the study is related to high pH leaching from the sample that creates an unfavorable condition for mold growth.

Table 3. Resistance to mold growth on the surface of fly ash-based geopolymers (GB) and PCB.

Material	Fungicidal zone, %		Fungicide resistance
	Before washing	After washing	
GB1	–	7.0	High
GB3	13.5	8.0	High
GB2	11.3	8.0	High
PCB	9.8	8.0	High

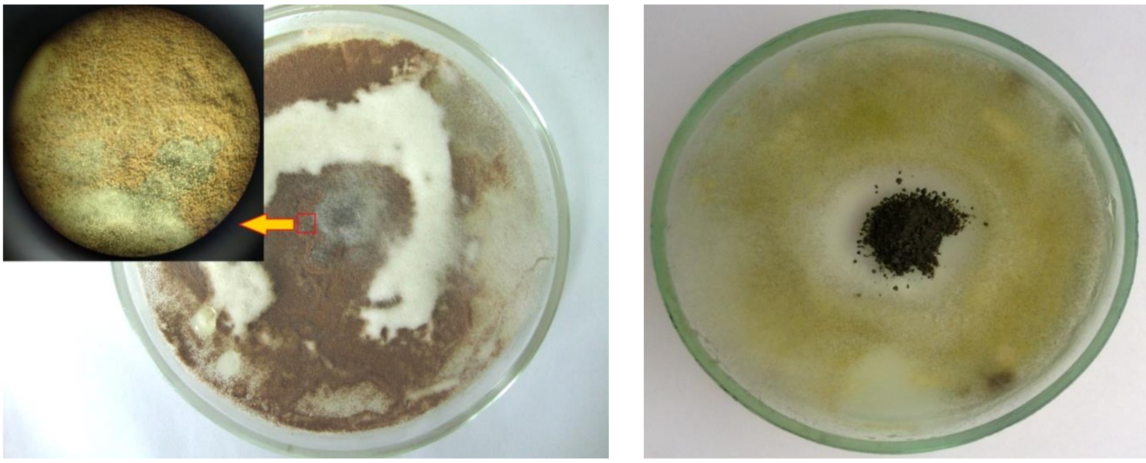

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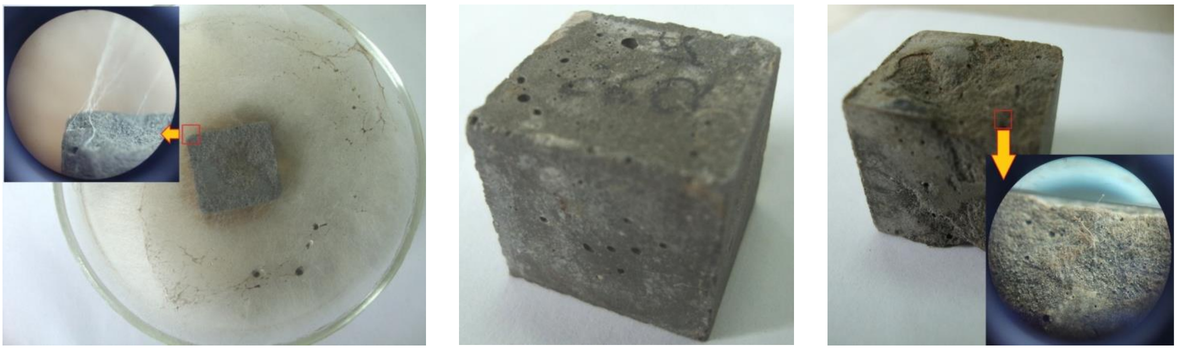
Figure 4. Mold growth on the surface of (a) FA3 and (b) not washed GB3

In order to eliminate the influence of high pH and, at the same time, focus on modeling the exploitation conditions when construction material has a long-term exposure to rain and ice water, the cubic samples of GB and PC binders washed in water for 72 hours with continuous stirring. After, the samples were soaked in the suspension of mold spores. After 28 days, all investigated samples were visually inspected and did not show any sign of mold growth on the surface observed with a naked eye (Figure 5).

It should be noted that with the reduction of pH level of crashed samples by washing with water, the fungicide zone around the samples was gone, however, the surface was still free of mold fungi. The fungicide zone for all investigated samples is compiled in Table 2. Interestingly, the mold fungi use solid samples just as mechanical support to further growth upward (Figure 5 a) as a more favorable environment for the microorganisms.



a b c

Figure 5. Different views of mold growth on the surface of water washed binder samples a) GB2; b) GB3; c) PCB

Visual inspection of the GB samples after exposure to a mold fungi media showed no apparent signs of bio-corrosion or any visual mold growth on the surface of the GB and PCB (Figure 5 b, c). Only by means of optical microscopy, insignificant mold growth was observed on the surface of one of the samples (GB2, GB3). Although, this phenomenon is yet to be investigated.

4. Discussion

The developed geopolymers demonstrated very low toxicity and leachability to the biota based on the low effect on germinating ability and growth retardation of the exposed oat seeds.

To a greater degree, this is observed for the fly ash product FA3, where the retardation effect achieves 19.3 %. The lowest or zero retardation effect among the studied fly ash products was observed for the FA1 and FA2.

The developed fly ash-based GB systems have demonstrated lower retardation effect on oat seeds growth, so, the E_r value for those ranges within 6.4 – 14.7 %. The highest value 14.7 % of Er in this study was observed for geopolymer composition GB1 and the lowest 6.4 % *Er* is for GB3.

Fungicide resistance test showed an intensive mold growth on the surface of the studied fly ash products which indicates a low bio-resistance and, therefore low toxicity with respect to microorganisms.

In the case of the fly ashes-based GB systems, the apparent absence of the *Aspergillus niger* mold fungi growth on the surface and a clearly defined fungicidal zone around the binder samples indicated their high fungicide resistance in terms of direct contact with microorganisms due to high pH of the binder systems. At the same time, the intensive population of the mold fungi around the studied samples confirms a low leachability of toxic components comprising fly ash products.

5. Conclusion

Overall results of the leachability and bio-resistance study showed that the developed binders using coal combustion products such as low-calcium fly ash products are eco-friendly materials towards biota, and, at the same time, appear a high fungicide resistance even for long-term exploitation. This outcome arises a particular interest in large-scale applicability of CCPs as cementitious binders, because up to 80 % of produced fly ash products have demonstrated to be safe for flora and fauna, and, therefore, can be readily utilized in the production of geopolymer binders.

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References

[1] Shekhovtsova J, Kearsley E P and Kovtun M 2016 Using fly ash in cement: cement & concrete *IMIESA* **41(2)** 67-8

[2] Strigáč J, Števulová N, Mikušinec J and Sobolev K 2018 The fungistatic properties and potential application of by-product fly ash from fluidized bed combustion *Constr. and Build. Mater.* **159** 351-60

[3] Alex T C, Kalinkin A M, Nath S K, Gurevich B I, Kalinkina E V, Tyukavkina V V and Kumar S 2013 Utilization of zinc slag through geopolymerization: Influence of milling atmosphere *Int. J. of Mineral Processing* **123** 102-7

[4] Ageeva M S, Shapovalov S M, Botsman L N and Ishchenko A V 2016 K voprosu ispolzovania promyishlennyih othodov v proizvodstve vyazhushchih veshchestv [Regards the use of industrial wastes in the production of binders] *Vestnik BGTU im V. G. Shukhova* [*Bulletin of BSTU named after V G Shukhov*] **9** 58-62 [In Russian]

[5] Mahdikhani M and Reza Khanban M 2019 Utilization of industrial waste residue containing heavy metals as a substitute for fine aggregates *Constr. and Build. Mater.* **221** 772-86

[6] Bulusu S, Aydilek A H, Petzrick P and Guynn R 2005 Remediation of abandoned mines using coal combustion by-products *J. Geotech. Geoenviron. Eng. ASCE* **131** 958-69

[7] Sapronova Z A, Sverguzova S V, Fomina E V and Fokina E V 2018 Carbonate-containing precipitate of sugar production from sugar beet as filler for polymer concrete *IOP Conf. Series: Mater. Sci. and Eng.* **365** 032042.

[8] Starostina I, Simonov M, Volodchenko A, Starostina Yu, Fomin A and E Fokina 2018 The usage of iron-containing sludge wastes in ceramic bricks production *IOP Conf. Series: Mater. Sci. and Eng.* **365** 032066

[9] Kozhukhova N., Kadyshev N, Cherevatova A, Voitovich E and Lushin K 2018 Reasonability of Application of Slags from Metallurgy Industry in Road Construction *Advances in Intelligent Systems and Computing* **692** 776-82

[10] Lesovik R V, Leshchev S I, Ageeva M S, Karatsupa S V and Alfimova N I 2015 The Use Of Zeolite-Containing Rottenstone Powder For The Composite Binding Production *Int. J. of Appl. Eng. Research (IJAER)* **10(24)** 44889-95

[11] Pedro Bolívar J, García-Tenorio R, Luis Mas J and Vaca F 2002 Radioactive impact in sediments from an estuarine system affected by industrial wastes releases *Environment Int.* **27(8)** 639-45

[12] Dawczyński S, Górskim M and Krzywon R 2016 Geopolymer as an alternative ecological material for buildings *14th Int. Conf. on New Trends in Statics and Dynamics of Buildings* (Slovakia, Bratislava)

[13] Duxson P, Provis J, Lukey G C and Van Deventer J S J 2007 The Role of Inorganic Polymer Technology in the Development of 'Green Concrete *Cem. and Conc. Res.* **37(12)** 1590-7

[14] Wei-Hao Lee, Ta-Wui Cheng, Yung-Chin Ding, Kae-Long Lin and Chun-Ping Huang 2019 Geopol-ymer technology for the solidification of simulated ion exchange resins with radionuclides *J. of Environmental Management* **235** 19-27

[15] Strigáč J and Martauz P 2016 Fungistatic properties of granulated blast furnace slag and related slag-containing cements *Ceramics-Silikáty* **60** 19-26

[16] Soebpong Tuntachon, Khanita Kamwilaisak, Theerasak Somdee, Wiyada Mongkoltanaruk, Vanchai Sata, Kornkanok Boonserm, Ampol Wongsa and Prinya Chindaprasirt 2019 Resistance to algae and fungi formation of high calcium fly ash geopolymer paste containing TiO_2 *J. of Build. Eng.* **25** 100817

[17] Habert G, d'Espinose De Lacaillerie J B and Roussel N 2011 An environmental evaluation of geopolymer based concrete production: reviewing current research trends *J. of Clean. Prod.* **19** 1229-38

[18] Rozineide A Antunes Boca Santa, Cíntia Soares and Humberto Gracher Riella 2016 Geopolymers with a high percentage of bottom ash for solidification/immobilization of different toxic metals *J. of Hazard. Mater.* **318** 145-53

[19] Kozhukhova N I, Zhernovsky I V and Strokova V V 2015 Evaluation Of Geopolymer Binders Biopositivity Based On Low-Calcium Fly Ash *Int. J.of Appl. Eng. Res.* **10(15)** 35527-9

[20] Kozhukhova N I, Lebedev M S, Vasilenko M I and Goncharova E N 2019 Toxic effect of fly ash on biological environment *IOP Conf. Series: Earth and Environmental Science (EES)* **272** 022065

[21] Kozhukhova N I, Lebedev M S, Vasilenko, M I and Goncharova E N 2018 Fly Ash Impact from Thermal Power Stations on the Environment *J. of Phys: Conf. Series* **1066(1)** 012010

[22] Sanjeet K, Verma Kripal Singh, Anand K Gupta, Vimal Chandra Pandey, Pragya Trivedi Rajesh and KumarVerma D D Patra 2014 Aromatic grasses for phytomanagement of coal fly ash hazards *Ecol. Eng.* **73** 425-8

[23] Strigácˇ J and Martauz P 2016 Fungistatic properties of granulated blast furnace slag and related slag-containing cements *Ceramics-Silikáty* **60** 19-26