PHYSICAL CHEMISTRY 2021

15th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume II

The Conference is dedicated to the

30th Anniversary of the founding of the Society of Physical Chemists of Serbia

and

100th Anniversary of Bray-Liebhafsky reaction

September 20-24, 2021
Belgrade, Serbia

Title: Physical Chemistry 2021 (Proceedings) **ISBN** 978-86-82475-40-8
Volume II: ISBN 978-86-82475-39-2
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski Trg 12-16, 11158, Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: ″Jovan″, <Printing and Publishing Company, 200 Copies
Number of pages: 6+388, Format A4, printing finished in December 2021

Text and Layout: ″Jovan″

200 - *Copy printing*

CONTENT

PHYSICAL CHEMISTRY 2021

15th International Conference on Fundamental and Applied Aspects of Physical Chemistry

Organized by

The Society of Physical Chemists of Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of Russian Academy of Sciences

and

University of Belgrade, Serbia:

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Table 1. Results of neurological (assessed by alterations in sensory-motor functions) and clinical tests scoring 24 h after treatments

Experimental group/test	I	Q	P1	P2	P3
Sensory- motor functions	100 ± 0.25	100 ± 0.25	98.31 ± 0.29	96.6 ± 0.48	94.92 ± 0.71
Clinical signs	-	-	-	-	-

CONCLUSION

Since MP have pervaded the ecosystems, exposure to these particles and their accumulation will probably only increase with time. Although acute MP exposure had no effect on sensory-motor functions and did not induced acute toxicity, due to reduced water and food intakes that are reported in current study, it can be assumed that MP might lead to health issues. Further research regarding pathologic mechanisms at cellular and tissue levels, as well as on the long-term effects of tissue accumulation, are necessary.

Acknowledgement

This work was supported by the Ministry for Science of the Republic of Serbia (451-03-9/2021-14/ 200175, 451-03-9/2021-14/ 200017 - 0902102 and 451-03-9/2021-14/ 200017 - 0902107).

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POTENTIAL USE OF SLAG GENERATED FROM LIGNITE COMBUSTION IN HITTING PLANTS

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ABSTRACT
This paper presents the examination of potential application of slag, obtained from lignite combustion process in heating plant in Valjevo, Serbia, as a replacement for cement in mortars and concrete production. Waste slag was characterized with X-Ray Diffraction Analysis, Field Emission Scanning Electron Microscopy and Gamma spectrometric analysis, while its application possibility was investigated with testing Pozzolan activity Strength activity index, Activity index and Water requirement. The aim of this study is to determine under what conditions the slag could successfully replace cement in construction industry in certain percentages. Based on presented results it was concluded that, after mixing with silicate fume, waste slag can be used for the purpose mentioned. Optimal proportion of cement replacement is 20%-: 18% of slag and 2% of silica fume.

INTRODUCTION
Coal is combustible dark-brown sedimentary rock of organic origin. Because of its capability to burn, it is used as a fossil fuel and represents a main source of energy in present-day society. It consists mostly of carbon and hydrocarbon, but also there are other elements such as sulphur, oxygen and nitrogen [1]. Coal is widely used for the purpose of electricity and heat generation, cement, steel, and alloys production as well as in other processes and industries.

Depending on the degree of coalification that has occurred, there are different types of coal: peat (precursor to coal), bituminous, subbituminous, lignite and anthracite, while the graphite known as "dead carbon" is the last grade of organic substance transformation of coal [2]. Coal Combustion Residues (CCRs) refer to the residues produced during the combustion of coal that include fly ash, bottom ash, slag, fluidized bed combustion ash and other solid fine particles [3].

In comparison with other types of coal, lignite has the lowest carbon content, therefore lowest calorific value and makes up the largest share of Serbian coal reserves. Despite its low quality, lignite is the most common fuel in Serbian heating facilities because of compatibility with present technology and is widely available with considerable price. In Serbia, heating plants supply about 25% of population with heat, which is generated from lignite combustion. However, these processes produce a lot of waste, such as slag and ash, which is followed by emissions of a number of harmful substances that potentially can cause substantial air, soil and water pollution. Some of them are sulfur and aluminum oxides as well as heavy metals such as wolfram, cadmium, lead, mercury, lime etc.

Slag is hard and durable waste matter with particles uniform in size and high resistance to surface wear, which contains different undesirable elements in small shares that can endanger the environment and cause population health issues. The use of waste slag in industry is currently in early phase in Serbia. Each year in Serbia millions of tons of slag and ash are produced in heating plants and disposed in landfills as waste products. Due to that the negative effects of their disposal in high amounts, environmental pollution is at increase in recent years. Reuse of waste slag in construction industry is of great potential and could come up as a possible solution for reducing the amount of waste disposed and, therefore its negative impact on environment. However, this aspect is still underdeveloped and not many studies were performed in this field. To derive the best possible way of slag usage, it must be examined and treated in accordance with results obtained.

In this study for the purpose of waste slag characterization, different physical – chemical and physical mechanical techniques were used: X-Ray Diffraction Analysis (XRD), Field Emission Scanning Electron Microscopy (FESEM), Gamma Spectrometry Analysis with gamma index determination and testing of the pozzolan activity.

METHODS

The slag samples were taken from landfill in Valjevo, Serbia. For further examination, samples were homogenized, dried and crushed so the particle size was 100% below 63□m. For assessment and monitoring of the phase composition of slag samples the X-Ray Diffraction Analysis (XRD) was used. The X-Ray diffract or Philips, PW-1710 with curved graphite monochrome and scintillation counter was used for investigations. Intensities of diffracted C_uK_α (λ=1.54178Å) were measured at room temperature in 0-02 °/s in range from 4 to 65 °2θ. Voltage of 40 kV and power of 30 mA was used for measuring. The morphology of the slag samples was determined on Tescan Mira 3 XMU field emission scanning electron microscopy (FESEM). The samples were coated with gold using sputter coater Polaron SC503 Fision Instrument prior to SEM analysis. For gamma-ray measurement, prepared sample of slag was placed in 125 ml PVC cylindrical box. The detector was calibrated using the coal and soil matrix in identical cylindrical boxes spiked with common mixture of gamma-ray emitters (^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, and ^{88}Y) certified by CMI [4]. The sample was measured in close to detector geometry by means of HPGe spectrometer - Canberra GX5019, with 55% relative efficiency and 1.9 keV resolutions for ^{60}Co at 1332.5 keV [5].

The gamma index (*I*) was obtained according to formula (1):

$$I = \frac{C(Ra^{226})}{300\ ^{Bq}/_{kg}} + \frac{C(Th^{232})}{200\ ^{Bq}/_{kg}} + \frac{C(K^{40})}{3000\ ^{Bq}/_{kg}} \qquad (1)$$

where C (Ra^{226}) is specific activity of Ra^{226} in Bq/kg, C (Th^{232}) is specific activity of Th^{232} in Bq/kg, and C (K^{40}) is specific activity of K^{40} in Bq/kg.

Preparation of the cement mixtures was conducted with addition of different amounts of the slag and silicate fume as it is presented in Table 1. Replacement of cement (in total) was: P 10 (10 %), P 15 (15 %), P 20 (20 %) and P 25 (25 %).

Pozzolanic activity was determined according to Standards SRPSB.C1.018, ASTM C311 - C311-13, EN 450-1, EN 450-1 Annex B, EN 196-3.

Table 1. Amounts of cement replaced with waste slag and silica fume

replacement cement	P 10	P 15	P 20	P 25
slag	9 %	13 %	18 %	22 %
silicate fume	1 %	2 %	2 %	3 %

RESULTS AND DISCUSSION

The sample of slag was examined with XRD Analysis on polycristal specimen (powder). The presence of minerals/phases such as: quartz, olivine, magnetite, pyrite, tridymite, feldspars was affirmed while the other minerals were less represented. Among feldspars, the most common were plagioclase feldspars, much more than alkali feldspars. Slag's degree of crystallinity was low [6].

FESEM analysis was used for examination of the slag morphology and surface properties. The micrographs were obtained with a magnification of 5000 and 40000x and are presented in Figure1. As it can be seen, slag is mainly constituted of irregularly shaped flat plates of different size of about up to □□m.

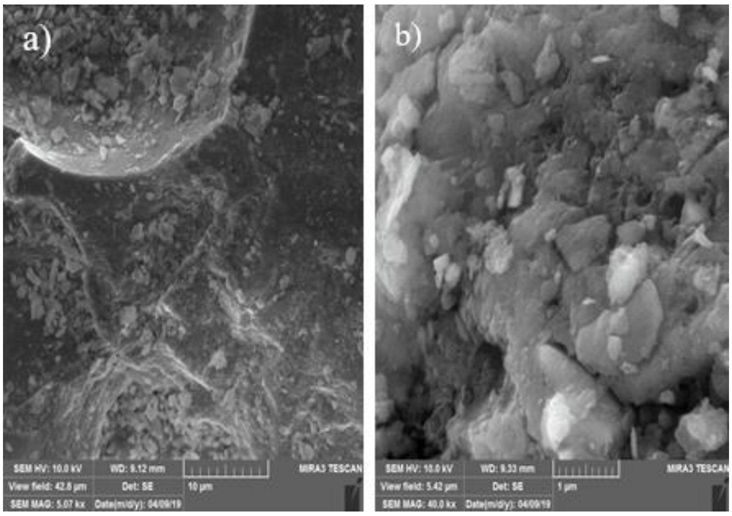

Figure 1. SEM photographs of slag sample taken with different magnification; a) 5.00kx and b) 40kx

Radiation risk by definition presents the probability for an individual to experience a certain harmful effect as a result of exposure to ionizing radiation. In order to assess the radiation risk, concentrations of activity of natural radionuclides Ra^{226} Th^{232} and K^{40} must be determined. The values of specific activity of certain radionuclides, obtained by gamma spectrometric analysis are shown in Table 2.

Table 2. Specific activity of radionuclides

Radionuclide	Specific activity (Bq/kg)
K^{40}	238 ± 12
Ra^{226}	88.3 ± 6.3
Th^{232}	65.9 ± 3.6

The gamma index (I) refers to the radiation dose, above the usual radiation exposure in the open space, in a building constructed of the material for which the index is calculated. The gamma index has a recommended limit value, I = 1, reported in Article 15 of the Regulation about limitations of radionuclides content in drinking water, foodstuffs, fodder, medicaments, items of general use, construction materials and other goods put in traffic. Based on the results of specific activity of radionuclides, gamma index was calculated using equation 1 and obtained value was I = 0.7. Therefore the gamma index of waste slag is under the recommended limit and does not represent a radiological risk on environment [7].

After characterization, waste slag was tested for application in cement industry as a replacement component in concrete and mortar production.

The analysed parameters included determination of activity index, water requirement, setting time and soundness. From results it can be concluded that parameters such as Initial and final setting time as well as Soundness satisfied criteria prescribed by the standards, while Strength activity index, Activity index and Water requirement do not satisfy requirements prescribed by the Standards. Namely, the values of Strength activity index (SAI) (28 days – 67 %) and Activity index (90 days - 76 %) were lower in comparison with Standard (Streingth activity (>75 % for 28 days) and Activity index for 90 days >85 %), while the value of Water requirement (113 %) was higher than value prescribed by the Standards ASTM C311-C311-13 and EN 450-1 (<95 %), what indicates that slag in present raw form could not be used as a cement replacement. Because of that additional actions were performed. Since it is well known that silicate fume possesses good pozzolanic properties, it was used as an addition to the slag in order to increase slags pozzolanic activity and improve its properties.

The results for samples Activity index with different slag and silicate fume ratios for 28 and 90 days are shown in Table 3. According to standard requirements (EN 450-1 p. 5.3.2), limit value for activity index for 28 days is 75%, and for 90 days is 85%. Values for all samples for 28 days were in intervals (82 ÷ 95) % and for 90 days in intervals (81÷93) %. Considering the goal of incorporating as much slag as possible, sample P 20, where the cement is replaced with 18 % slag and 2 % silicate fume had a best performance.

Table 3. Activity index of mixed samples of slag and silicate fume

Activity index							
P 10		P 15		P 20		P 25	
28 days	90 days	28 days	90 days	28 days	90 days	28 days	90 days
95 %	93 %	91 %	89 %	87 %	85 %	82 %	81 %

CONCLUSION

XRD analysis showed that the slag sample mostly appears in amorphous form and possess very low crystalline. According to FESEM analysis it can be concluded that the surface of slag mainly is consisted of irregularly shaped particles with the diameters mainly of 1 μm. Radiological examination presented that gamma index of analysed slag sample was 0.7 which is not of radiological risk for the environment.

Results based on overall analysis of slag samples from heating plant in Valjevo, Serbia indicate that slag in raw form doesn't show pozzolan activity since Strength activity index (SAI), Activity index, and Water requirement do not meet criteria prescribed by the standards. As a solution, the silicate fume was added to the slag, which enhanced its characteristics.

From presented results, it may be suggested that the waste slag could be used in construction industry, as a cement replacement in mortars and concrete production, but only after addition of the silica fume. Results showed that it is justified to replace cement with slag in the amount up to 20 %. In that case, the ratio of the constituents in the mixture is: cement/ slag/ silica fume = 80/18/2 %.

Acknowledgement

The research was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia.

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CIP - Каталогизација у публикацији
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544(082)
66.017/.018(082)
502/504(082)
343.98(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (15; 2021; Beograd)

Physical Chemistry 2021: proceedings: the Conference is dedicated to the 30th Anniversary of the founding of the Society of Physical Chemists of Serbia and 100th Anniversary of Bray-Liebhafsky reaction. Vol. 2 / 15th International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 20-24, 2021, Belgrade, Serbia; [organized by The Society of Physical Chemists of Serbia in co-operation with Institute of Catalysis Bulgarian Academy of Sciences ... [et al.]]; [editors Željko Čupić and Slobodan Anić]. - Belgrade: Society of Physical Chemists of Serbia, 2021 (Belgrade: Jovan). - VI str., str. 347-732: ilustr.; 30 cm

Tiraž 200. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-82475-39-2
ISBN 978-86-82475-40-8 (niz)

а) Физичка хемија -- Зборници б) Наука о материјалима -- Зборници в) Животна средина -- Зборници г) Форензика -- Зборници

COBISS.SR-ID 53325065