Effective Cement Binders On Fly And Slag Waste From Heat Power Industry Of The Primorsky Krai, Russian Federation

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Abstract: The research paper deals with the prospects of using fly ash and slag waste from the heat power industry of the Primorsky Krai, Russian Federation as an effective filler for composite cement binder. An integrated assessment of the possibility of using this industrial waste is based on the results of studying its microstructure, the assessment of its radioactive background, and the results of X-ray phase and differential thermal analyses, as well as morphological characteristics of the particles.

Index Terms: Fly Ash and Slag Waste, Primorsky Krai, Construction, Composite binder, Concrete.

1. INTRODUCTION

One of the urgent problems accompanying the production of cement binder, which is the basis of structural concrete products used in the construction industry, is a significant cost of raw materials and energy per unit of the finished product. To ensure the marketability of products, enterprises need to switch to the development and use of advanced energy-saving and resource-saving technologies based on the use of industrial waste. The solution to this problem is also very important for accelerating the socio-economic development of the Russian Far East, which is reflected in the relevant legislative acts of the Government of Russia [1], [2], [3], [4], [5]. According to the data of the Russian Federal State Statistics Service in the Primorsky Krai and the report of the Russian Union of Cement Producers, there was an increase in the cement production from 5 % to 10 % in 2018-2019. To manufacture concrete products, 3.5 million tons of cement together with natural mineral admixtures consisting of sand (400 thousand cubic meters), crushed stone (2 million cubic meters), and limestone (18 thousand cubic meters) are used annually in the Primorsky Krai [6], [7], [8]. It should be noted here that using the abovementioned natural aggregates for the manufacture of concrete products significantly increases their cost due to the limited quantity of non-metallic building materials in the region, the remoteness of deposits from the final consumer, and poor transport infrastructure [9]. Researchers in Russia and worldwide recommend using fly ash and slag waste as an active mineral admixture in the production of cement binders to reduce financial expenses [10], [11], [12]. Fly ash and slag are common large aggregate industrial wastes from thermal power enterprises with reserves amounting to hundreds of million tons. The energy industry in the Primorsky Krai is focused on the use of fossil coal and as a result, fly ash and slag landfills occupy an area of 22,000 hectares [13], [14]. The aim of the research carried out by the authors is to develop the composition and technology for manufacturing a composite binder using fly and slag waste components. In this paper, the authors examine the physicochemical properties of waste, which are necessary to assess the effectiveness of its use for the manufacture of a binder with cement (or clinker). The subject of the research is the fly and slag waste from ash-disposal areas of three thermal power plants located in the Primorsky Krai, Russian Federation (the Vladivostok TPP-2, Artyom TPP, and Partizansk GRES).

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2 RESEARCH MATERIALS AND METHODS

A total of 50 samples of fly ash and slag waste were collected from 1 m depth along a rectangular grid with a step of 30 meters. The coordinates were recorded using a navigation system. Point samples were collected from one or more layers at test sites. A combined sample was made by mixing at least five samples taken at the same site. The mass of each spot sample was at least 500 g. The mass of the combined sample was 5 kg. The samples were analyzed using the following scientific equipment:

1) The microstructural analysis was carried out using the scanning electron microscope JSM-6490LV (Jeol, Japan) and the automated system for measurement of particle size, shape and chemical identity Morphology G3SE-ID (Malvern Panalytical, United Kingdom);

2) The X-ray diffraction analysis was carried out using the X-ray fluorescence spectrometer ARL Quant'X (Thermo Fisher Scientific, USA);

3) The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out using the Thermoscan-2 equipment (Analit Teplo Control, Russia).

3 RESULTS AND DISCUSSIONS

When using fly ash and slag waste, it is necessary to consider that fossil coals are sorbents capable of accumulating various chemical elements, including radioactive ones. In this regard, the issue of assessing the radiation safety of these wastes in the production of various commercial products is quite relevant. The main elements than determine the radioactivity of materials are the isotopes of thorium (232Th), uranium (238U), radium (226Ra), their radioactive products, and potassium isotope (40K) [15]. The radioactive properties of fly ash and slag waste from Russian TPPs [16] and the concentration of radionuclides in them are presented in Table 1 and Table 2.

TABLE 1

ANALYSIS OF CENTRIFUGAL CONCENTRATOR OPERATIONS ON BENEFICIATION OF MICRODIPERSED GOLD FROM DREDGING TAILINGS

Line No.	Sample No.	Sample name	C_{Au}, [g/t]	σ_{chgd}, [g/t]
1	Sample 1	Initial sample of technogeneous waste from placer mine "Pad Shirokaya" (dredging tailings PGSH 50)	< 0,2	± 0,11
2	Sample 2	Concentrate derived from sample No.1 via modification of CC No.1 before modernization.	0,294	± 0,2
3	Sample 3	Concentrate derived from initial sample after the first benefication via CC-M	37,0	± 0,7
4	Sample 4	Magnetic faction derived from Sample 4 after magnetic separation using PBM-32/20	2,1	±0,1
5	Sample 5	Non-magnetic faction derived from Sample 5 after magnetic separation using PBM-32/20	31,9	±4,2
6	Sample 6	Concentrate derived from Sample 5 after secondary benefication using CC-M	234,0	±39,2
7	Sample 7	Tailings derived from Sample 5 after secondary benefication using CC-M	21,0	±3,0

TABLE 2

CONCENTRATIONS OF RADIONUCLIDES IN COALS, SLAG, AND FLY ASH FROM THERMAL POWER PLANTS, BQ/KG

Изотоп	Уголь	Шлак	Летучая зола
Уран ^{238}U	9-31	56-185	70-370
Радий ^{226}Ra	7-24	20-166	85-281
Торий ^{232}Th	9-19	59	81-174
Калий ^{40}K	26-130	230-962	233-740

As can be seen from the data presented, the content of uranium and thorium increases in coal combustion products, but the concentration of elements does not exceed the threshold values for materials that are allowed for use in the residential and public construction (class I) in the Russian Federation [17]. The data provided in [18] (Table 3) allow us to conclude that the fly ash and slag waste obtained by burning the Far Eastern coals does not constitute a radiation hazard. One of the characteristics of fly ash and slag waste, which determines the possibility of their use as a binder component, is the hydraulic activity.

TABLE 3

THE SPECIFIC EFFECTIVE RADIATION ACTIVITY OF FLY ASH AND SLAG WASTE, DEPENDING ON THE COMPOSITION

Наименование показателя	Результат измерения (А), Бк/кг		
	Владивостокская ТЭЦ-2	Артемовская ТЭЦ	Партизанская ГРЭС
Активность ^{40}K	362±89	342±68	516,9±101
Активность ^{232}Th	31,5±19,7	29,5±15,7	193,2±22,3
Активность ^{226}Ra	37,63±6,32	27,23±5,93	113,1±6,37
$A_{эфф} = A_{Ra} + 1{,}31A_{Th} + 0{,}085A_K$	80±30	93±20	>360

This activity is based on the chemical interaction of silicon and aluminum oxides with calcium hydroxide. Calcium hydroxide is released during the hydration of clinker minerals forming calcium hydro silicates and hydro aluminates, which determines the strength of the cement brick.

TABLE 4

ANALYSIS OF CENTRIFUGAL CONCENTRATOR OPERATIONS ON BENEFICIATION OF MICRODIPERSED GOLD FROM DREDGING TAILINGS

	Уголь	Теплоэлектростанция		
		Владивостокская ТЭЦ-2	Артемовская ТЭЦ	Партизанская ГРЭС
	Преобладающий тип угля	Приморский бурый (Павловский разрез)	Каменный	Нерюнгринский каменный
Содержание элементов в расчете на оксиды, %	SiO_2	63,0	48,1	47,4
	TiO_2	0,5	0,0	0,9
	Al_2O_3	21,4	29,3	22,3
	Fe_2O_3	7,5	6,5	19,6
	CaO	3,4	9,7	4,8
	MgO	2,1	1,8	2,8
	K_2O	1,3	1,2	0,1
	Na_2O	0,3	0,2	0,4
	SO_3	0,6	2,3	1,62
	$CaO_{св}$	0,4	<0,1	Нет

The composition and structure of fly ash and slag waste depend on a set of simultaneous factors: the type and morphological features of the combusted fuel, the fineness of grinding during fuel preparation, the chemical composition of the mineral part of fuel, the temperature in the combustion zone, and the time period for which the particles remain in the combustion zone, etc. According to the microstructural analysis, more than 80 % of fly ash and slag wastes are heterogeneous, highly dispersed, vitrified spherical particles with different grain sizes (Figure 1).

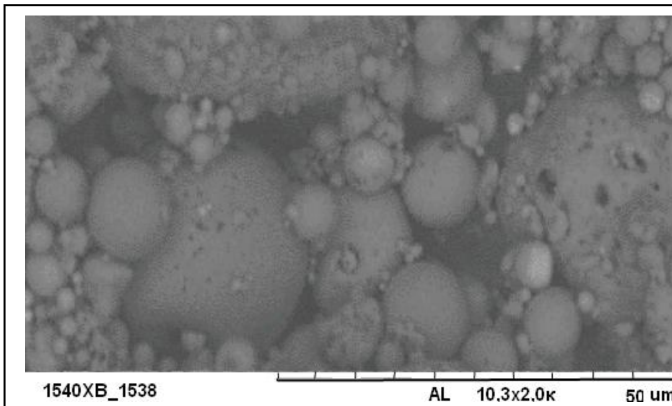

Fig. 1*. The microstructure of fly ash and slag waste from the Vladivostok TPP-2 (magnification × 2000)*

The highly dispersed structure of fly ash and slag waste is a factor in predicting the activity of particles during hydration in relation to the binder components. According to the data [19], the vitreous phase, the proportion of which depends on the combustion conditions and the fuel used, is represented by X-ray amorphous aluminosilicate compounds (Table 4).

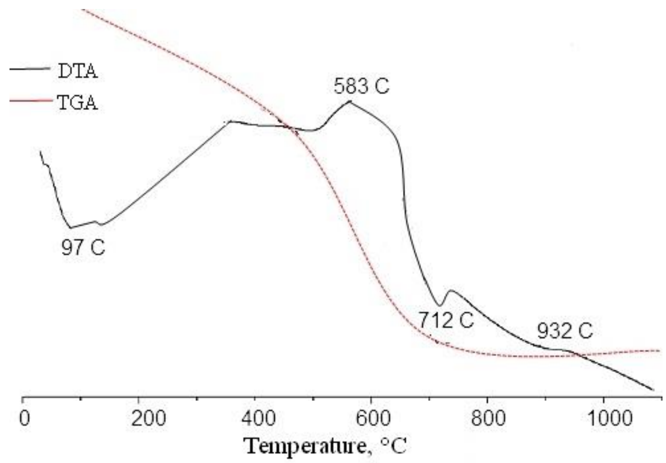

***Fig. 2**. The results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of fly ash and slag waste*

An intense andeffect coupled with the mass loss at 500-700°C indicated the burn-off of residual fuel consisting of coal particles and residues of coke and char. A moderate exothermic effect reaches its peak at 932°C and reflects the crystallization of mullite-like compounds in the aluminosilicate phase [20]. According to the results of X-ray phase analysis, diffractive crystalline reflections of the mullite phase, in addition to quartz, were identified in the fly ash (Figure 3).

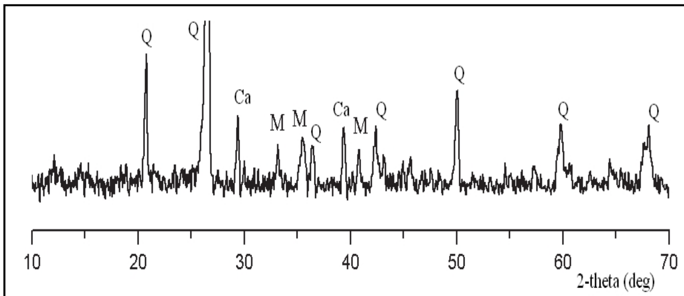

***Fig. 3**. The results of X-ray phase analysis of fly ash and slag waste from the Vladivostok TPP-2 (Q – quartz, Ca – calcite, M - mullite)*

In summary, the investigated fly ash is represented by aluminosilicates by 80-90 %, about 2/3 of which are silicon oxides. The fly ash comprises of crystalline and amorphous phases. The crystalline phase is represented by quartz, feldspars, mullite, etc., while the amorphous phase is represented by glass.

5 CONCLUSIONS

The results of our analyses allow us to draw some conclusions of interest for this study:

1. In terms of the radiation hazard, the fly ash and slag samples meet the requirements of regulatory and technical documentation of the Russian Federation in the field of construction. The fact that the specific effective activity of fly ash and slag waste in the Primorsky Krai does not exceed 370 Bq/kg, allows us to treat this waste as the first-class building materials suitable for all types of construction.

2. Due to their high dispersion ability and mineral composition, fly ashes of thermal power plants in the Primorsky Krai can exhibit hydraulic activity during chemical interaction with calcium hydroxide formed during the hydration of cement clinker. This has a positive effect on the strength of the cement brick.

Based on the presented results, we can conclude that fly ash and slag waste from the heat power of the Primorsky Krai, Russian Federation can be recommended as an effective mineral admixture in the production of cement binder for the construction industry.

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REFERENCES

[1] A. Teara, “The use of waste materials for concrete production in construction applications”, IOP Conference Series: Materials Science and Engineering, vol.342 (1), 012062, 2012.
[2] J. Bolden, “Utilization of recycled and waste materials in various construction applications”, American Journal of Environmental Sciences, vol. 9 (1), pp. 14-24, 2013.
[3] V.G. Puzach, “Nanomodified concrete based on cement and cementless binders with the use of ash and slag waste from thermal power plants”, Nanotechnology, vol.3, pp. 30-33, 2012.
[4] “On Approving the Strategy for Spatial Development of the Russian Federation for the Period Up to 2025”, Order to the Government of the Russian Federation No-207-r, http://www.consultant.ru/document/cons_doc_LAW_318094 2019.
[5] “On approval of the state program of the Russian Federation “Socio-economic development of the Far Eastern Federal District”, Decree of the Government of the Russian Federation N 308, https://base.garant.ru/70644078 2014.
[6] “Primorye in numbers: A brief statistical compilation”, Primorskstat, 2019.
[7] “Cement review”, Soyuzcement, https: //www.eurocement.ru/engine/documents/document15791.pdf 2019.
[8] Office of the Federal Antimonopoly Service in the Primorsky Territory, https://primorie.fas.gov.ru 2019.
[9] “Report on the results of the analysis and assessment of the competitive environment in the commodity market of non-metallic building materials in the territory of the Primorsky Territory”, Office of the Federal Antimonopoly Service in the Primorsky Territory, https://primorie.fas.gov.ru/analytic 2019.
[10] R. Hidayawanti, “The efficiency of fly ash and cement slag to development building”, IOP Conference Series: Materials Science and Engineering, vol. 365 (3), 032040, 2019.
[11] M. Makarova, “Application of ash and slag wastes in the production of building materials”, IOP Conference Series: Materials Science and Engineering, vol. 365 (3), 032040,

2018.
[12] N.I. Buravchik, "Astringents based on technogenic raw materials", Ecological Bulletin of Russia, vol.5, pp. 28-33, 2014.
[13] L.N. Alekseiko, "The economic prospect of processing ash and slag waste from coal-fired power plants in the Far Eastern region", Bulletin of the Far Eastern State Technical University, vol.3 (5), pp. 61-80, 2010.
[14] L.N. Alekseiko, "On the integrated processing of ash and slag waste from energy", Ecology and development of society: proceedings of the IX Int. conf. - International. Academy of Sciences of Ecology, Human and Nature Safety, pp. 12-21.
[15] Z. Shen, "Radioactivity of five typical general industrial solid wastes and its influence in solid waste recycling", Minerals, vol.9 (3), pp. 168, 2019.
[16] Ya.E. Yudovich, "Toxic elements-impurities in fossil coals", http://en.bookfi.net/book/484490 2005.
[17] "Building materials and products. Determination of the specific effective activity of natural radionuclides", GOST 30108-94, http://docs.cntd.ru/document/871001235 1994.
[18] L.T. Krupskaya, "The content of natural radionuclides in the Far Eastern coals and ash and slag waste of thermal power plants", Proceedings of universities. Mountain Journal, vol. 1, pp. 51-53, 2007.
[19] V.O. Batarshin, "Particularly heavy concrete for special purposes", Fundamentals of building materials science Collection of reports of the International online congress, pp. 258-267, 2017.
[20] R. Fediuk, "Increase in composite binder activity", IOP Conference Series: Materials Science and Engineering, vol. 156 (1), 012042, 2016.