Journal of Physics: Conference Series

PAPER • OPEN ACCESS

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To cite this article: N I Kozhukhova *et al* 2018 *J. Phys.: Conf. Ser.* **1066** 012010

FLY ASH IMPACT FROM THERMAL POWER STATIONS ON THE ENVIRONMENT

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Abstract. Dumps of thermal power plants in Russia occupy significant areas. They are a source of pollution of air and water basins, contribute to increasing groundwater salinity and falling into the environment of radioactive elements. The work presents the results of experiments to identify the physical and chemical properties and toxicological effect of low-calcium ash from five thermal power plants on the environment.

One of the most significant sources the environment contamination are large-tonnage solid wastes from thermal power plants (TPPs). Therefore, in a number of regions these dumps have significantly complicated the ecological situation. Considering that a significant part of the country's electricity (about 70%) is produced by burning solid fuels, the increase in ash and slag wastes is expectedto be continue in the future. One of the less-demanded species of ash storage facilities is fly ash - fine-disperselow-calcium wastes obtained as a result of burning of coal fuel. They are characterized by inertness to water, therefore they can'tbe used as a hydraulic binding component in the construction industry. At present time, the examples of low-calcium fly ash are almost absent [1–3].The total volumeof utilization of these by-product does not exceed 7–10% [4]. Storage of accumulating fly ash in open areas may cause a negative impact on the ecosystems of nearby territories and the ecological situation as a whole [5].

Earlier, the authors studied different fly ash from Russian and foreign producer in terms of their availability as environmentally friendly raw materials [6, 7]. The biotesting methods used in the work demonstrated a positive or neutral effect on bioobjects, however, at the same time, significant differences in the effect depending on the producer of fly ashwere fixed, the reason of which have not been practically studied at present.

In this paper, the results of studies on the identification of physical and chemical characteristics and toxicological effect of fly ash on the environment were presented.

To determine the causes of toxicity of water extracts of fly ash, the determination of pH-value, total hardness, dry residue, which characterizes the presence of soluble salts in the filtrate, the composition of the residual ash after filtration. All listed indicators are environmental factors in watermedium, the effect of which on biological systems is the main factor.

The measurement of the pH-value was carried by ionomer pH-150M («Gomel Plant of Measuring Instruments»). The chemical composition of the dry residues from the aqueous extracts was determined withan energy-dispersive spectrometer based on a high-resolution scanning electron microscope TESCAN MIRA 3 LMU and a FTIR spectrometer VERTEX 70 (Bruker Optics) (absorption spectra of tablets of materials with potassium bromide in an average IR-region 370-4000 cm^{-1}).

Chemical composition of the studied fly ash before and after treatment in water medium as well as qualitative mineral composition of dry residue were determined with XRF-analysis using spectrometer ARL 9900 WorkStation («Thermo Fisher Scientific»).

The study was carried out for five low-calcium fly ash from Russian(1–3) and foreign (3, 4) thermal power plants. As a reference, the Portland Cement CEM 42.5N (Belgorodsky cement company, Russia) was used.

According to Russian Standard GOST 30108-94 andthe Norms of Radiation Safety (NRB-99/2009), a concentration of natural radionuclidein the used fly ashes islow and they can be use for all types of construction.

When measurement of pH-value of water extracts from fly ash, an increase in alkalinity was observed for all the samples vs. medium (pH> 8.23). This indicates that used fly ash contains soluble alkaline components varied in a wide range with a minimum content for fly ash 3 (pH 8.37), and maximal for Portland cement (pH 12.55). It is due to the presence of calcium hydroxide. The pH-value of the water extracts for fly ash 1, 2, 4, 5 is higher than for fly ash 1 (pH 9,00-9,33).

The degree of hardness of water extracts, i.e. the concentration of alkaline-earth metal ions in the composition of fly ash is capable of affecting the life activity of bioorganisms. The highest hardness of water extracts was observed for fly ash 4 and 5: 15.2–17.1 mg-equ/L. Other extracts from fly ash had a total hardness from 4.8 to 6.9 mg-equ/L.

Expect for the total content of salts, elemental composition is also important (Table 1).

Table 1. Elemental composition of dry residues from water extracts

Fly ash	Content of chemical elements, weight %											
	O	Ca	Mg	Na	K	S	C	Cl	N	Si	F	Al
1	19.8	5.0	2.6	16.1	3.2	4.7	16.1	31.8	–	0.6	0,1	0.1
2	35.3	7.1	6.4	5.0	5.3	6.1	10.3	19.8	1.5	2.6	0,4	0.1
3	36.8	7.1	5.8	6.1	3.7	5.0	8.7	21.3	3.4	1.6	0,6	–
4	45.7	15.7	0.7	4.0	1.7	14.1	13.0	4.3	–	0,7	–	0,1
5	40.5	10.8	0.5	7.0	1.3	9.7	22,3	7.2	–	0.2	–	0.1
Reference	11.7	16.4	0.1	5.4	10.7	1.5	9.3	44.8	–	0.1	–	0.1

The obtained results indicate the presence of elements such as S^{6+}, C^{l-}, C^{4+}ions, as well as N^{6+}, F^{+7}, P^{+5} ions, which are typical for an acid residue.Also the presence of alkaline cations such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}takes place. The high content of Na^{+} and Cl^{-}ions negatively effect on life activity ofbioorganisms.

The significant differencein elemental composition of the dry residues is associated with different intensity ofions removal from the fly ash. In addition, the effect of atmospheric precipitation on dumps was simulated by long-term treatment in water medium of waste with distilled water.

According to the obtained results, significant decrease of $SO_3$and CaOin fly ash after washing was observed. (Table 2). Concentrationsofother oxidesarechangedslightlyordoesnotchanged.

The most significant decrease in the mass content of sulfur oxides occurs on fly ash 4 and 5. This is due to the presence of sulfates in the dry residue, which is confirmed by the data obtained (Fig. 1).

According to the results of IR-spectroscopy, for all dry residues, the content of sulfates, predominantly calcium, and various modifications thereof was observed, for example, gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 0.5H_2O$) - vibrations of SO_4^{2-} groups with characteristic absorption bands at 601, 660, 668, 1096, 1118, 1140, 1150 cm^{-1} and structural OH^- groups with absorption bands at 1620, 1686, 3243, 3406, 3492, 3547, 3608 cm^{-1}) (Fig. 2). In Portland cement, carbonates were detected (peaks at 710, 874, 1405 cm^{-1}). The presence of chlorides with IR-spectroscopy is very difficult to detect.These salts are mostly transparent in the infrared range, they can be detected by sorbtive water, but the presence of other crystalline hydrates makes this task more complicated. However, they were detected with qualitative XRF-analysis (Fig. 2).

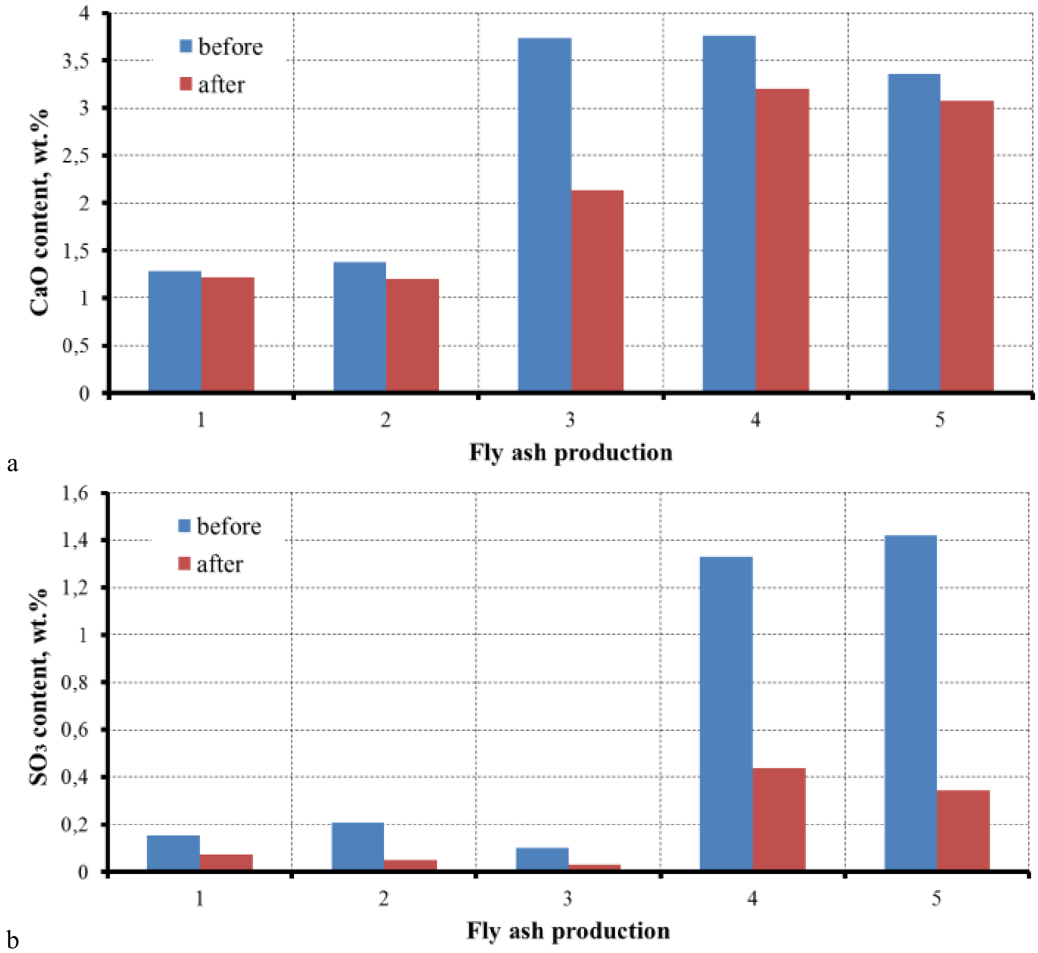

Figure 1. Content of CaOand SO_3 oxides in fly ash before and after long-term treatment in water medium

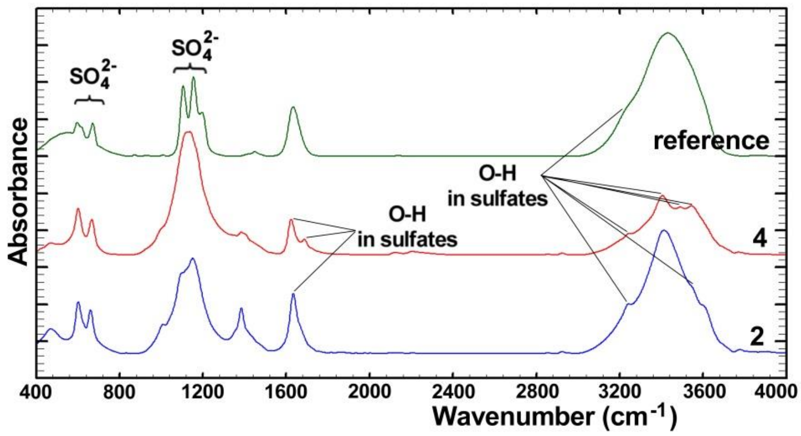

Figure 2. IR-spectra of dry residues of water extracts

In particular, halite is one of thecomponents in all water extracts. Potassium chlorides and magnesium were in samples of fly ash 1–3 were detected. In dry residuesof fly ash 4 and 5 (Fig.3), the predominance of sulfates, mainly gypsum, was observed. The appearance of the reflection forsassolite (H_3BO_3) is associated with a small amount of studied material for test and its extra contentwhen the sample preparation (Fig. 3).

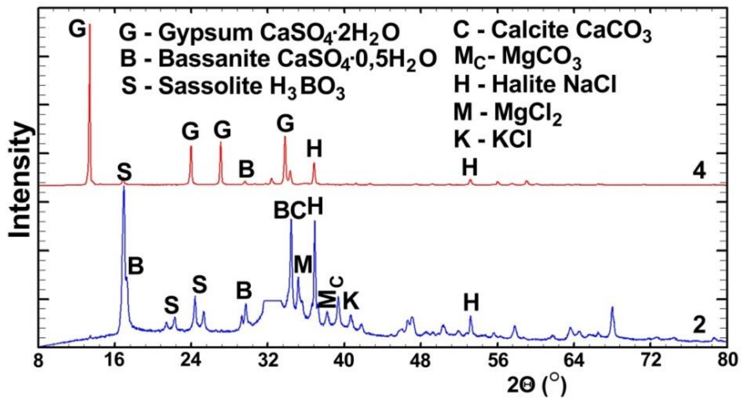

Figure 3. X-ray patterns of dry residues from water extracts

The dry residues from water extracts for fly ash 1–3 the crystals of sodium, magnesium and potassium chlorides, and less extent of carbonates and sulfatetake place (Fig. 3).Chemical composition of dry residues from fly ash 4 and 5 is characterized by the predominance of calcium sulfates and less of chlorides.

As shown in [5], under natural water exposure, the elements of fly ash those are negative for bioorganisms are removed from fly ash. According to the obtained results of biotest of water extracts, using Daphnia magna Straus crustaceans as the test objects for toxicity determination demonstratea dramatic increase inmortality of daphnia (more than 90%) with a reduction of their lifetime (not more than 24 hours). A high concentration of leached salts from water extracts of fly ash can initiate a high mortality of daphnia. Experiments carried outwith other test organisms demonstrated the same results.

Thus, as a result of the experiments was the fly ash from foreign producers (4, 5) more significantly affected the environment vs. fly ash from Russian producers (1–3).pH-valuefor water extract from fly ash 1–3 are close to neutral.The least amount of leached salts and average value of hardness are also typical for this fly ash.

Acknowledgments
This research work is financially supported by Ministry of Education and Science of Russian Federation in framework of State Assignment №11.9329.2017/8.9, using equipment of High Technology Center at BSTU named after V.G. Shoukhov.

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