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# Toxic Effect of Fly Ash on Biological Environment

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**Abstract.** Class F fly ash is non-demand mineral by-product from fuel industry that is stored in landfills polluting a surrounding territories. Content and composition of soluble mineral components in fly ashes from different power plants are varied in wide range. Leaching into fly ashes these component can differently effect on bioobject activity. In this paper correlation between pH-value of water extracts from fly-ashes, hardness of them and content of evaporated mineral residue from the water extract was studied. It is determined the increasing of evaporated mineral residue content corresponds to increasing of hardness and pH-value of water extracts.

## 1. Introduction

These guidelines, written in the style of a submission to J. Phys.: Conf. Ser., show the best layout for your paper using Microsoft Word. If you don't wish to use the Word template provided, please use the following page setup measurements. Annually world-wide a huge emissions of solid powder-like mineral wastes from power plants, such as fly ash into bio environment takes place, impacting a negative effect on flora and fauna. Finally, we have global changes in hydrobiological cycle and gas balance in atmosphere.

Whereas a lot of investigations devoted to ecological production, recycling and utilization of fly-ash it is major problem at present.

Methods of reduction of trace element leaching from fly ashes [1] as well as conservation of radioactive element [2] by zeolitization of them are proposed

Limited usage of industrial mineral wastes, for instance, as raw materials in construction industry, generally associated with following two factors:

- inadequacy in quality according to Safety Standards like sanitary-hygienic standards, standard of environmental management, radiation safety standards etc. explains a necessity of immediate waste immobilization and deposition [3].
- insufficient knowledge about the waste characteristics prevent to forecast its effect on natural environment when real usage.

Among of low-demand by-products the mineral wastes such as low-calcium fly ashes (Class F) produced by power plants using a coal fuel take a large part [4]. Earlier the potential of Class F fly ashes from different power plants as ecological source was studied [5].

Results of applied biotesting methods was found, the Class F fly-ashes generally slightly effect on microorganisms, higher plant and aquatic fauna but hydrobionts *Daphnia magna*, which demonstrate



mortality growth in fly-ash water extracts. The dependence of effect on hydrobionts activity of fly ash type was confirmed. But it is necessary to provide better understanding of this phenomenon to determine an environmental friendliness of fly ash at initial stage of choice of raw materials for construction composites.

There are a few studies in agriculture field concerning any effect of fly ash on biota. Parab N and Sinha S. [6] found the fly ash amendment significantly improved the physical and chemical properties of soils that promote to plants growth and yield.

Negative influence of natural radionuclides (NRN) content in coal sources and based fly ash on surrounding soils and groundwater was reported by Rogacheva S.L. [7] and Belyakova Zh.S etc. [8]. But not only NRN in fly ashes effect on life activity of bioobjects. Nevertheless, information about this problem is not sufficient.

This research is focused on effect of mineral component in Class F fly ash on life activity of bioobjects. Five types of fly ashes from different power plants were used. Explanation of toxic effect of fly ashes was based on the following studied parameters of water extracts from them: pH-value and hardness; composition and content of residue, indicating on available of soluble salts. Above parameters are keys ones for bioobjects.

## 2. Materials and methods

Free Russian Class F fly ashes (FA1–FA3) and two U.S.'s ones (FA4–FA5) were used in this study. Portland cement CEM I 42,5N («Belgorodsky cement» company, Russia) as a reference material was used throughout all experiments.

pH-values of water extracts from the studied fly ashes and Portland cement was determined with ionomer pH-150 .

Hardness of the experimental water extracts was measured according to Russian Standard 31954–2012 [9], based on data of concentration of Ca<sup>2+</sup>, Mg<sup>2+</sup> ions leached out from experimental fly ashes when water extract preparation.

Initially, 20 g of each fly ash as well as Portland cement was placed in flasks containing 200 g of aerated water, stirred for 72 hours and setting-out for 2 hours. Then water extract (liquid phase) was separated from insoluble solid residue with filter paper.

Then 50 ml of each water extract was placed in 250-ml flask followed by adding of 2.5 ml of ammonium standard buffer with pH=10 and 3–4 drops of dark-blue chrome as pH-indicator and mixing. The obtained composition was titrated against 0.05N solution of Trilon B (versene) until decolouration effect achievement (from pink to blue-purple). Hardness of water extracts (H, mg-eq/l) was calculated by following:

$$H = 1000 \cdot \frac{V_1 \cdot c}{V},$$

where V<sub>1</sub> – volume of 0.05N solution of Trilon B, required for titration, ml; c – normal concentration of Trilon B solution (0.05N), mg-eq/l; V – volume of water extract, required for titration, ml

Content of evaporated residue from water extracts (mg/l) was determined after evaporation of water extract in oven until constant weight using the following equation:

$$x = \frac{(a - b) \cdot 1000}{V},$$

where a – mass of cup, containing evaporated residue, mg; b – mass of cup without of evaporated residue, mg; V – volume of water extract, ml.

*Chemical composition of fly ashes as well as insoluble residues* obtained after the water extract preparation was accomplished by XRF-analysis with spectrometer ARL 9900 WorkStation (Thermo Fisher Scientific).

*Characteristics of evaporated residues* were determined with energy-dispersive X-ray spectrometer X-MAX 50 (Oxford Instruments NanoAnalysis), IR-Fourier spectrometer VERTEX 70 (Bruker Optics).

Quantitative XRD-analysis was realized with spectrometer ARL 9900 WorkStation using database PDF-2 (ICCD).

### 3. Results and discussion

Data of  $\text{pH}$ -values for the water extracts demonstrate the presence of soluble salts in fly ashes and concentration of them strongly influence  $\text{pH}$ -value of water medium when its interaction. Correlation between  $\text{pH}$ -value and toxic effect is high due to presence of soluble components like ammonium salts, hydrogen sulphides, sulphides, cyanides. This factor can be basic to effect on life activity of bioobjects. So,  $\text{pH}$ -values of the water extracts obtained by above described method were measured (Table 1).

**Table 1.**  $\text{pH}$ -values of water extracts from studied materials.

No	Water extracts from	$\text{pH}$ -value
1	Aerated water	8.23
2	FA1	9.22
3	FA2	9.00
4	FA3	8.37
5	FA4	9.33
6	FA5	9.27
7	Portland cement	12.55

Data from Table 1 demonstrate the water aeration leads to increasing of  $\text{pH}$ -value. It can be connected with removal of  $\text{Cl}^-$  ions and  $\text{CO}_2$ -oxide.  $\text{pH}$ -parameter is varied in wide range from  $\text{pH}=8.37$  for FA3 to  $\text{pH}$  12.55 for Portland cement. This parameter for FA1, FA2, FA4, FA5 is higher ( $\text{pH}=9.00\text{--}9.33$ ) vs. FA3. All water extracts are characterized by higher  $\text{pH}$ -value vs. aerated water ( $\text{pH}>8.23$ ) due to presence of alkali-ions.

Earlier study [5] reported the most favorable environment  $\text{pH}$ -value for activity of hydrobionts *Daphnia Magna* is varied within 7.2–8.5. Higher  $\text{pH}$ -value initiates toxic effect of soluble mineral component containing in fly ashes leading to death of them. So, it demonstrates negative effect of fly ashes on bioobjects being in environmental media.

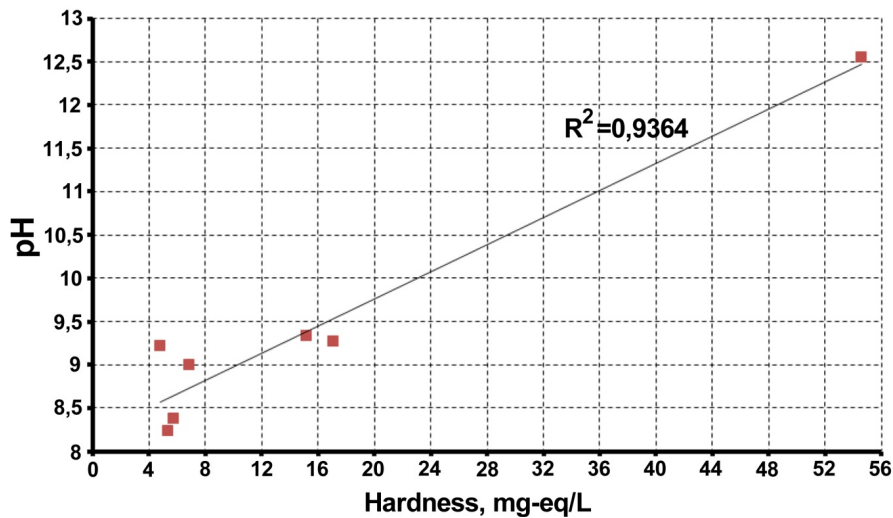
Hardness of water extracts from the fly ashes is total concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions in carbonates, hydrocarbonates, sulphates, chlorides, nitrates, phosphates and silicates as well as concentration of metals.

The highest hardness is typical for Portland cement based water extracts (54.6 mg-eq/l) and the lowest – for FA1-based water extract (4.8 mg-eq/l), that is presented in Table 2.

**Table 2.** Characteristics of water extracts.

No	Water extract from	Content of evaporated residue, mg/l	Hardness, mg-eq/l	$\text{pH}$ -value
1	Aerated water	708	5.4	8.23
2	FA1	1033.9	4.8	9.22
3	FA2	1171.8	6.9	9.00
4	FA3	891.8	5.8	8.37
5	FA4	2335	15.2	9.33
6	FA5	2607.8	17.1	9.27
7	Portland cement	4771	54.6	12.55

Table 2 and Fig. 1 demonstrate quite good correlation between  $\text{pH}$ -values and hardness of water extract.

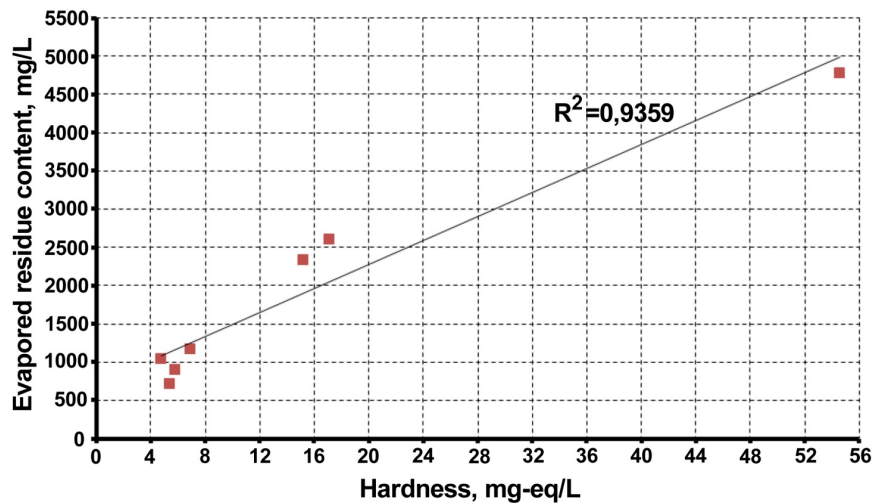


**Figure 1.** Correlation between pH-values and hardness of water extract.

High values of hardness and pH for Portland cement are associated with presence of cations of alkaline-earth metals in salts, oxides and hydroxides.

Hardness of water extract is strongly connected with content of soluble mineral components (salts) in evaporated residue (Table 2).

Content of evaporated residue allows estimation of quantity of residue soluble mineral components, as well as correlation of one with hardness of water extracts (Fig. 2).



**Figure 2.** Correlation between content of evaporated residue and hardness of the water extracts.

According to Fig. 1 we can observe the higher content of evaporated residue correspond to higher hardness value.

According to A.M. Ovchinnikov [10], water extracts from FA1, FA2, FA4, FA5 are weakly-mineralized. Water extracts from FA3 and aerated water are related to high-salt waters. Water extract from Portland cement is salt brine. So, high concentration of soluble salts can be one of the negative factors for activity of bioobjects, initiating death of them.

High-salt water reacts with inorganic components forming insoluble complexes that reduce toxic effect of them on bioobjects. In contrast, weakly-mineralized water provides a good solubility of mineral components leading to increasing of toxic effect. Presence of  $\text{Ca}^{2+}$  ions in water medium decrease permeability of biological membranes, preventing toxicant penetration into bioorganisms.

### 3.1. Chemical characteristics of evaporated residues

Elementary composition is also very important for evaporated residues from fly ashes. Data in Table 4 demonstrate a presence of  $S^{6+}$ ,  $Cl^-$ ,  $C^{4+}$ ,  $N^{4+}$ ,  $F^{7+}$ ,  $P^{5+}$  ions that are responsible for acidity water extract. Also there are  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  that are responsible for alkalinity.

In compliance with [11] a high concentration of  $Na^+$  and  $Cl^-$  provides not good environment for bioobjects activity.

**Table 4.** Elementary composition (wt. %) of evaporated residues.

Water extract from	O	Ca	Mg	Na	K	S	C	Cl	N	Si	F	P	Sr	Al
Aerated water	37.3	11.4	4.3	7.9	4.8	10.3	7.3	12.4	1.5	2.8	0.1	–	–	0.03
FA1	19.8	5.0	2.6	16.1	3.2	4.7	16.1	31.8	–	0.6	0.1	–	–	0.1
FA2	35.3	7.1	6.4	5.0	5.3	6.1	10.3	19.8	1.5	2.6	0.4	0.2	–	0.1
FA3	36.8	7.1	5.8	6.1	3.7	5.0	8.7	21.3	3.4	1.6	0.6	–	–	–
FA4	45.7	15.7	0.7	4.0	1.7	14.1	13.0	4.3	–	0.7	–	–	–	0.1
FA5	40.5	10.8	0.5	7.0	1.3	9.7	22.3	7.2	–	0.2	–	–	0.1	0.1
Portland cement	11.7	16.4	0.1	5.4	10.7	1.5	9.3	44.8	–	0.1	–	–	–	0.1

Significant variation in elementary composition of evaporated residues (Table 4) allows reporting different degree of ions removal from fly ashes.

Comparison of chemical characteristics of fly ashes before and after water treatment demonstrates dramatic decreasing of  $SO_3$  ions and CaO (Table 5).

**Table 5.** Chemical characteristics of fly ashes before and after water treatment.

Oxides content, wt. %	Fly ashes									
	FA4		FA5		FA2		FA3		FA1	
	1 <sup>a</sup>	2	1	2	1	2	1	2	1	2
$SiO_2 + Al_2O_3 + Fe_2O_3$	89.04	90.48	89.69	90.64	94.57	94.44	91.9	89.46	94.47	94.49
TiO <sub>2</sub>	1.07	1.07	1.07	1.07	1.10	1.06	0.97	1.22	1.17	1.12
MgO	0.80	1.45	1.04	1.43	0.55	0.69	1.00	3.05	0.577	0.743
CaO	3.76	3.2	3.36	3.07	1.38	1.2	3.74	2.13	1.28	1.22
Na <sub>2</sub> O	0.64	0.778	0.87	0.782	0.64	0.793	0.63	0.91	0.52	0.557
K <sub>2</sub> O	1.68	1.67	1.65	1.65	0.64	0.638	0.65	2.33	0.75	0.73
P <sub>2</sub> O <sub>5</sub>	0.33	0.525	0.48	0.529	0.54	0.576	0.36	0.428	0.48	0.476
SO <sub>3</sub>	1.33	0.438	1.42	0.344	0.209	0.049	0.102	0.03	0.153	0.072

<sup>a</sup>1 – before water treatment; 2 – after water treatment

The highest reducing of  $SO_3$  ions is typical for FA4 and FA5 that explain sulfates present in evaporated residues (Table 5).

IR-spectroscopy was realized with KBr-bearing pellets in frequency region of 370–4000  $cm^{-1}$ . All the obtained IR-spectra for evaporated residues demonstrate vibrations of  $SO_4^{2-}$ -group at 601, 660, 668, 1096, 1118, 1140, 1150  $cm^{-1}$  and O-H-group at 1620, 1686, 3243, 3406, 3492, 3547, 3608  $cm^{-1}$  (Fig. 3). According to [12–17] it is associated with presence of gypsum ( $CaSO_4 \cdot 2H_2O$ ) and bassanite ( $CaSO_4 \cdot 0.5H_2O$ ). In IR-spectrum for Portland cement based evaporated residue there are peaks at 710, 874, 1405  $cm^{-1}$  responsible for carbonates [13, 14].

It is difficult to recognize chlorides with IR-spectroscopy due to invisibility of them in IR-band. It can be identified by absorbed water only, among others crystalline hydrates.

Identification of chlorides presence was realized with XRD-analysis (Fig. 4). Gallite is detected for all water extracts. Calcium chloride and magnesium chloride present in FA1–FA3. For FA4 and FA5 a high concentration of sulfates like gypsum is typical. Presence of sassolite ( $\text{H}_3\text{BO}_3$ ) is associated with using of them when the samples preparation.

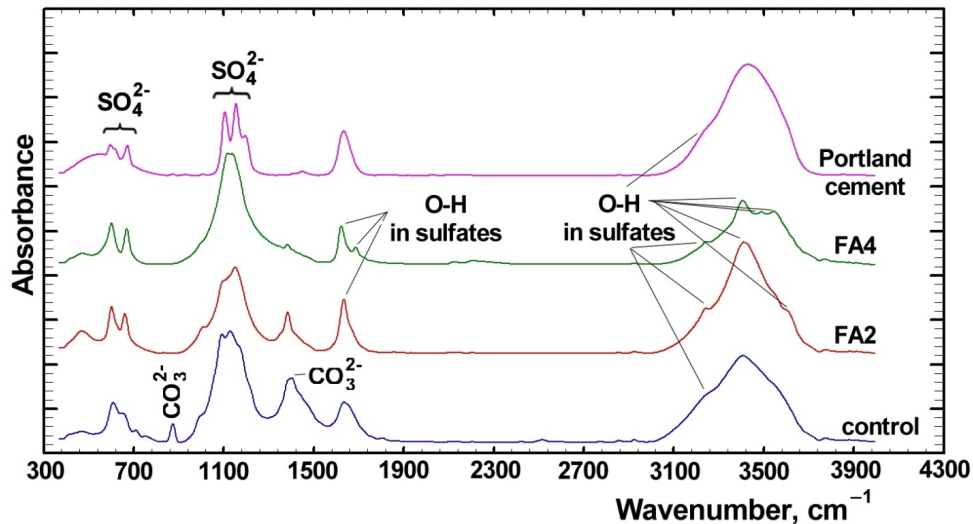


Figure 3. IR-spectra of evaporated residues.

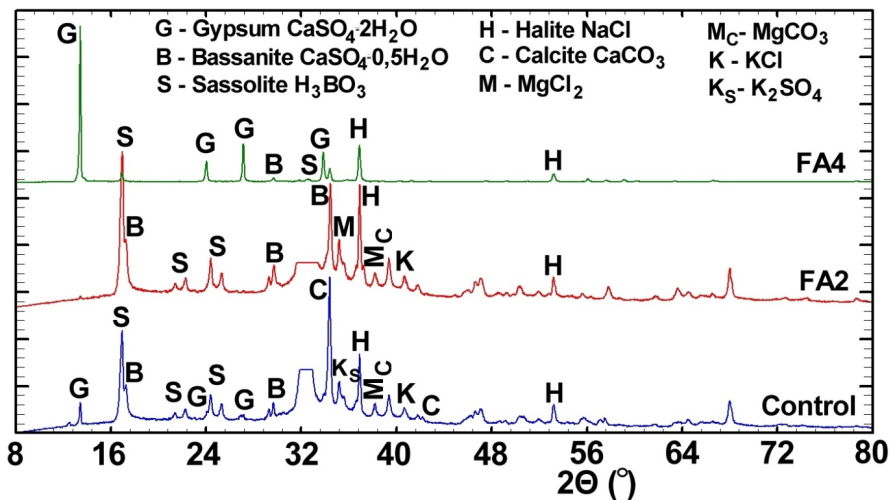
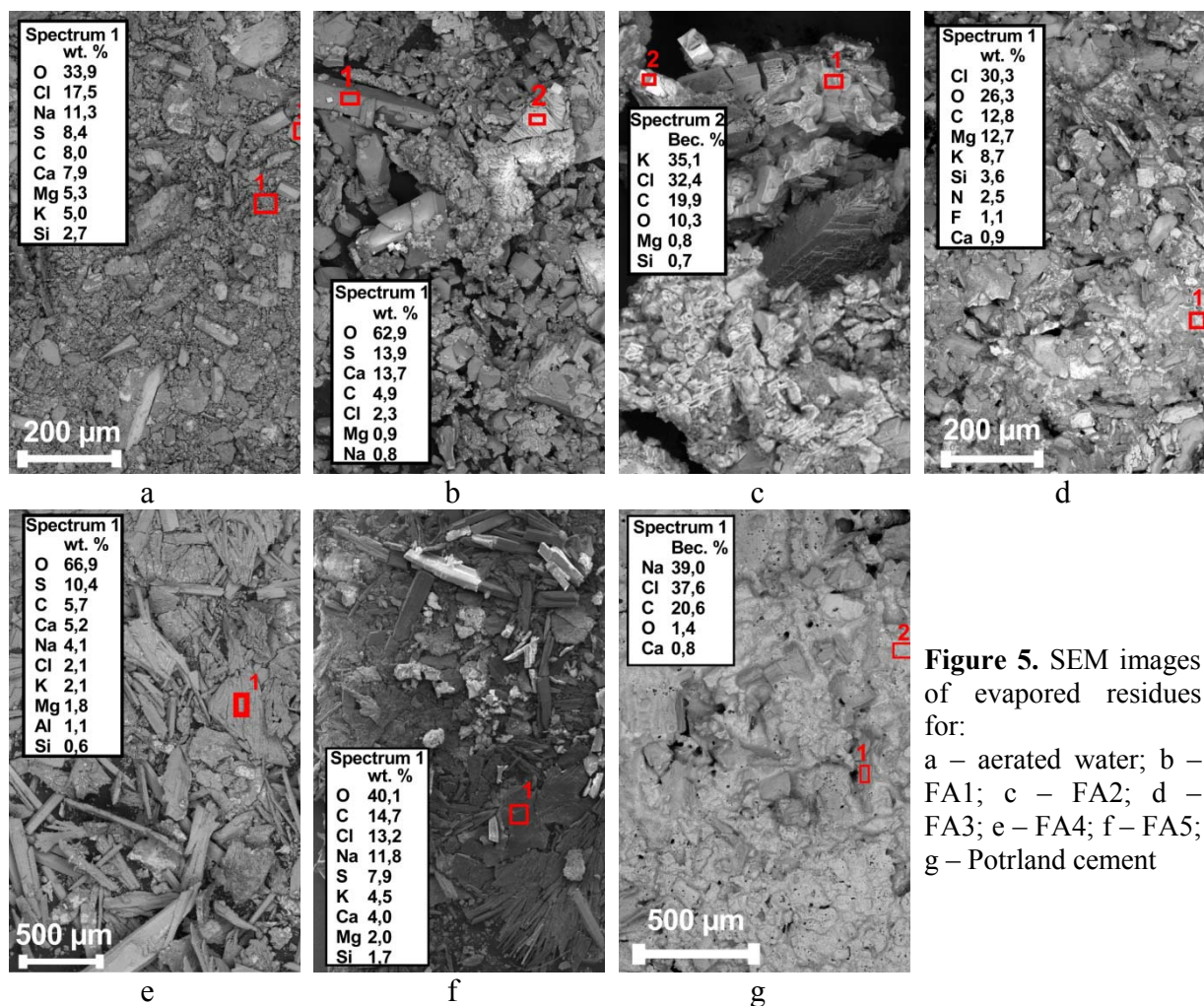


Figure 4. X-ray powder diffraction patterns of evaporated residues.

SEM-images for evaporated residues confirm a presence of chlorides, carbonates and sulfates widely varied in different samples (Fig. 4).

According to SEM-image the evaporated residue from Portland cement generally consists of sodium and potassium chlorides (Fig. 5g, Spectrum 2) and calcium chloride as product reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{HCl}$  (Fig. 3, 4, 5e, Spectrum 1; Fig. 5f, Spectrum 1). Also we can observe a presence of carbonates and sulfates (Fig. 3, 4, 5a, Spectra 1 and 2).

Evaporated residues from FA1–FA3 also contain crystals of sodium chloride (Fig. 5b, Spectrum 2), magnesium chloride and potassium chloride (Fig. 5c, Spectra 1 and 2; Fig. 5d, Spectrum 1) and less content of carbonates and sulfates (Fig. 4, 5b, Spectrum 1; Fig. 4d, Spectrum 2). Evaporated residue from FA4–FA5 is characterized by high concentration of calcium sulphates (Spectra 1 and 2), Fig. 5f, Fig. 5g, Spectrum 2) and less content of chlorides (Fig. 3, 4, 5f, Spectrum 1; Fig. 5g, Spectrum 1).



**Figure 5.** SEM images of evaporated residues for: a – aerated water; b – FA1; c – FA2; d – FA3; e – FA4; f – FA5; g – Portland cement

As far as bioobjects like *Daphnia magna* are very sensitive to variation of chemical composition of life environment. It can reduce life activity and die under effect of salts of magnesium, potassium, sodium and calcium as well as  $Zn^{2+}$  and  $Cu^{2+}$  ions, sulfide and hydrogen sulfide.

#### 4. Summary

Higher pH-values for all water extracts vs. aerated water takes place due to presence of soluble alkaline components varied in wide range from pH=8.37 for FA3 to pH=12.55 for Portland cement associated with calcium hydroxide presence. pH-values for FA1, FA2, FA4, FA5 are in range of 9.00–9.33.

It is determined the hardness of water extracts as indicator of concentration of alkali-earth metal ions negatively effect on life activity of bioobjects in water medium.

Data of hardness for the water extracts have a good correlation with chemical characteristics of evaporated residues. High concentration of soluble salts in FA4, FA5 and Portland cement explains a high depth level for *Daphnia magna* [5].

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