ISSN 0027-1314, Moscow University Chemistry Bulletin, 2014, Vol. 69, No. 5, pp. 229–234. © Allerton Press, Inc., 2014.
Original Russian Text © A.A. Sedova, V.M. Ivanov, V.P. Selyaev, R.A. Polyanskov, A.K. Osipov, L.I. Kupriyashkina, 2014, published in Vestnik Moskovskogo Universiteta. Khimiya, 2014, No. 5, pp. 301–307.

Studying the Processes of Damage to Cement by Solutions of Carboxylic Acids

A. A. Sedova[a], **V. M. Ivanov**[b], **V. P. Selyaev**[a], **R. A. Polyanskov**[a],
A. K. Osipov[a], **and L. I. Kupriyashkina**[a]
[a] *Ogarev Mordovia State University, Saransk, Republic of Mordovia, Russia*
[b] *Department of Chemistry, Moscow State University, Russia*
e-mail: sandro@analyt.chem.msu.ru; polyanskov_aleks@mail.ru

Received April 15, 2014

Abstract—The interaction of the solutions of certain carboxylic acids with filled cement composite has been studied via the static contact of phases. Damage to materials made up of zeolite rocks (ZRs) with cement binders during interaction with aggressive media has been analyzed.

Keywords: cement stone, carboxylic acid, zeolite rocks, precipitate, structure, kinetic curves, strength

DOI: 10.3103/S002713141405006X

INTRODUCTION

The building sector has been developing rapidly over recent years. The production of various types of concretes possessing specified sets of operational and physical–mechanical characteristics is developing particularly rapidly. Here, processes for the manufacture of concretes based on the economy of both material and energy resources is gaining crucial importance. Research associated with the development of the formulations of concretes providing the reduction in the consumption of cement is promising [1].

Zeolite rocks (ZRs), which make it possible to improve a series of properties of concretes by 20–30% along with increasing the economy of cement manufacture, are finding a wide application in the production of construction materials. The corrosive resistance, frost resistance, and strength have increased substantially [2]. ZRs are widely abundant in the Republic of Mordovia. Their low price and high adsorption and ion-exchange properties make it economically feasible to use them in the building sector [3].

The aim of this work is to study the processes of interaction of cement filled with ZRs in solutions of tartaric, citric, and oxalic acids, which mimic the processes of biodeterioration of concretes, using the methods of analytical chemistry. The problem of the damage of construction materials under the action of aggressive media is very pressing at present. Thus, the colonies of various microorganisms that settle on the surface of the concrete not only have a negative influence on the aesthetics of the premises or wall constructions but also promote the destruction of concretes [4].

Low-molecular carboxylic acids, which are exuded in fairly large amounts, are characteristic products of the metabolism (vital functions) of microorganisms settling on the surface of the concrete. They form an acidic film, the pH of which depends on the nature and structure of the acid, on the surface of the concrete. The interaction of carboxylic acids with the concrete results in the release of calcium, magnesium, and iron ions from it as well as complexation reactions on the surface of the micropores of the concrete, which widen and deepen with time, which gradually triggers the process of destruction of the structure of the material.

The aim of this work is to study the processes taking place in cement model solution of the carboxylic acid system.

EXPERIMENTAL

Reagents, solutions, and instrumentation. Solutions of analytical grade carboxylic (tartaric, citric, and oxalic) acids at 0.5, 1.0, and 2.0% were prepared by dissolving the weighted amounts of these acids, which were preliminarily dried at 150°C for 1 h, in distilled water. The concentration of the carboxylic acids was determined by an iodometric method [5].

Stock standard solutions of Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+ salts were prepared from State Standard Samples (SSS) each containing 1 mg/mL of the corresponding ion. The solutions were diluted with deionized water and 0.1 M HNO_3 on the day of the analysis for the experiments on the atomic absorption spectrophotometer [6].

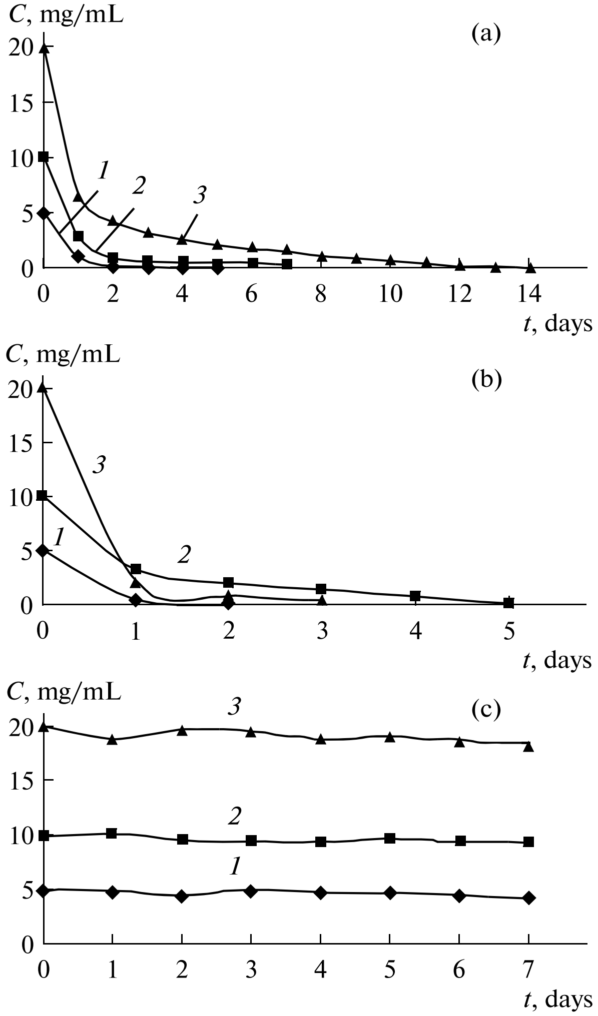

Fig. 1. Change in concentration of (a) tartaric, (b) citric, and (c) oxalic acids (initial concentrations of (*1*) 0.5, (*2*) 1.0, and (*3*) 2.0% as a function of time of contact with cement filled with the ZR (10% filling, grain size of ZRa 0.315 mm).

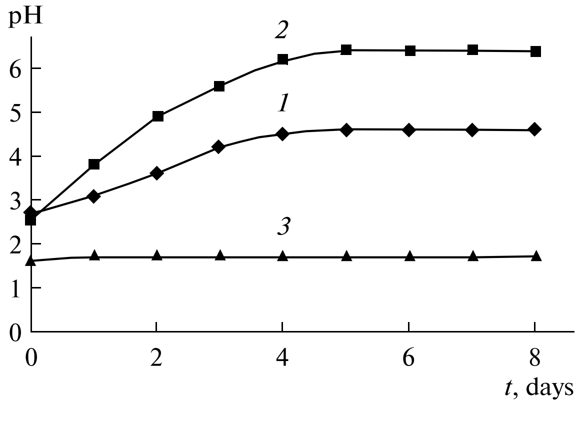

Fig. 2. Time history of medium pH for eight days during exposure of cement filled with ZR in 0.5% solutions of (*1*) tartaric, (*2*) citric, and (*3*) oxalic acids (the degree of filling of the cement stone with the ZR is 30%, the grain size is 0.315 mm).

The concentrations of Ca^{2+}, Mg^{2+}, K^+, and Na^+ ions in the test solutions were determined using ion chromatography on a Shimadzu PIA-1000 ion analyzer [7]. The concentration of Fe(III) and Al(III) was determined using an atomic absorption method with electrothermal atomization on a Shimadzu AA-7000 atomic absorption spectrophotometer [8]. The acidity of the solutions was monitored potentiometrically using an Expert–pH pH meter [9].

The strength of the cement composites was measured using a destructive method. The elemental analysis of the precipitates isolated from the cement stone during the exposition in the solutions of tartaric and citric acids was performed by an energy-dispersive X-ray method. The structure of the precipitates was studied using a Quanta 200i 3D FEI multi-purpose scanning electron microscope [10].

RESULTS AND DISCUSSION

Prepared on the basis of M400 Portland Cement, cement composites filled with ZRs from the Atyashevskoe deposition (Republic of Mordovia) with a degree of fill of 10, 20, and 30% and a dispersive capacity of 0.315, 0.63, and 1.25 mm were exposed to 0.5, 1.0, and 2.0% solutions of tartaric, citric, and oxalic acids mimicking the processes of biodeterioration. The type and character of the C_{HA}–*t* (d) and pH–*t* (d) kinetic dependences were determined.

The C_{HA}–*t* (d) kinetic curves give the evidence of the fact that, during contact of the cement with tartaric and citric acids, the concentration of tartrate and citrate ions decreased notably over 5–14 days and then the concentration of the listed ions decreases to the minimum. The results of the analysis are presented in Figs. 1a and 1b.

The C_{HA}–*t* (d) kinetic curves for oxalic acid of the same concentration differ greatly from curves with tartaric and citric acids. Only an insignificant decrease in the concentration of oxalate ions was observed during an eight-day-long cement stone–oxalic acid contact. The results of the analysis are presented in Fig. 1c.

The pH–*t* (d) kinetic curves for tartaric and citric acids differ from the similar kinetic curves for oxalic acid. A monotonic increase in the pH of the reaction mixture (the decrease in the acidity of the contacting solution) is observed in the plots of the pH–*t* (d) dependence for tartaric and citric acids (Fig. 2). This is explained by the interaction of tartaric and citric acids with the cement and the washout of Ca^{2+} ions contained in it into the aqueous solution. In citrate solutions, the pH of the medium is higher than that in the tartrate solutions, which gives the evidence of its higher activity.

We monitored the coloring of the solution and the appearance of the cement stone during the experiment. The solutions of tartaric and citric acids turned yellow–green. The deepening of the coloring occurred with the increase in the duration of the cement stone–tartaric acid and cement stone–citric acid contacts and with the increase in the concentration of the acids. A colored film that gradually peeled off and changed into a precipitate formed on the surface of the cubes of the cement in both cases. It can be supposed that citric acid affected the cement stone and washed out the Ca^{2+}, Fe^{3+}, and Al^{3+} ions more actively. Tartaric acid was less active compared to citric acid, but the pH of the medium increased substantially as well. The coloring of the solutions occurred due to the formation of the complex compounds of Fe(III) with the chelating acids.

No substantial decrease in the concentration of oxalate ions during the contact of the cement stone with oxalic acid was observed. No coloring of the solutions and no formation of stains on the cubes of the concrete were observed and no precipitates were formed as opposed to tartaric and citric acids. The acidity of the medium changed insignificantly and was within a pH range of 1.5–1.8.

Oxalic acid differs from the other acids considered in terms of strength ($pK_{a1} = 1.25$), which gives the evidence of its high degree of dissociation. Here, more hydroxonium ions are formed, that is why the pH of the medium is lower when compared to the citrate and tartrate solutions. On the other hand, the low solubility of calcium oxalate apparently promotes the formation of a protective film of the aforementioned compound formed during the interaction of oxalic acid with the Ca^{2+} ions washed out from the concrete on the surface of the concrete.

Such compounds are also formed with tartaric and citric acids but they are more soluble. The increase in the solubility takes place due to the formation of the complex compounds of calcium with tartrate ($\beta = 62.89$) and citrate ($\beta = 1\ 481$) ions [11]. Oxalate ions exhibit a much smaller capability to form soluble complexes with Ca^{2+} ions when the solubility product is low [11, p. 253]: $K_S\,(CaC_2O_4 \cdot H_2O) = 2 \times 10^{-9}$.

The protective film formed by the compounds of oxalic acid apparently assists the maintenance of the low pH value on the surface of the concrete as well as the delay in the formation of microcracks and, possibly, an increase in the waterproofing of the concrete.

The active acidity of the medium is an important factor for the growth and development of microorganisms causing biocorrosion. Most of them grow better in low-acid media (pH of 5.0–6.0). Overly acidic or alkaline media are toxic for the majority of microorganisms. The limiting pH values, over and below which the growth of the colonies of microorganisms stops, are 11.0 and 1.0, respectively. A low pH value (1.5–1.8) is maintained in the system of cement and oxalic acid within the range of the studied concentrations. This hampers the growth of microorganisms.

After 5–14 days, the cement was separated from the model solutions and dried in air and then in a drying oven at 60–90°C. The cement composites were tested for strength and the content of Ca^{2+}, Mg^{2+}, K^+, and Na^+ ions in the filtrate was determined using a method of ion chromatography. The content of Fe^{3+} and Al^{3+} was determined using an atomic absorption method. The precipitate isolated from the filtrate was dried and studied on a multi-purpose scanning electron microscope with an integrated focused ion beam system.

The results of the analysis of the filtrate are presented in Table 1. It may be concluded that filtrates contain Ca^{2+} ions in large quantities along with Fe^{3+} and Al^{3+} ions. The content of the aforementioned components in the filtrates depends on the nature of the carboxylic acids, their concentration, and the degree of fill of the composites with ZR. The higher the fill of the composite with ZR, the higher the content of Ca^{2+} in the filtrate. Here, the content of Ca^{2+} is higher than that of Mg^{2+}, which is in accordance with the elemental analysis of the ZR. The content of Ca^{2+} ions in the filtrates of tartaric acid is higher than that in the presence of citric acid. The smallest amount of free Ca^{2+} ions is contained in those filtrates, where the cement rock contains 30% ZR, which corresponds to the elemental composition of the ZR. Here, a great role is assigned to the state of the ZR, namely, to the grain size. The grain size affects the adsorption of the CaC_2O_4 low-soluble compound. The smaller the grain size, the larger the surface of the ZR and the higher the absorption. However, when the content of the filler is high (30%), its negative influence on the concrete becomes more pronounced, namely, a decrease in the water resistance and the segregation of the banding clay takes place, which induces a reduction in adsorption and, hence, a decrease in the strength of the concrete.

The elemental composition of the precipitate on the cement in the cement and tartaric acid and cement and citric acid systems was determined using scanning electron microscopy. The results of the analysis (Table 2) give evidence of the fact that the precipitate was formed mostly by calcium compounds. Here, the content of CaO depends on the concentration of tartaric and citric acids. Generally, the content of CaO increases with the increase in the degree of filling of the ZR to 30% of the mass of the cement stone. Magnesium oxide was only found in several precipitates and in relatively small quantities. The precipitates also contain Al_2O_3, Fe_2O_3, and SiO_2. A method of crystalline microchemical analysis made it possible to elucidate the structure of the precipitates, which depended on the composition of the composite, the part of the ZR in it, and concentration of the acid, in which the composite was exposed. Figure 3 shows the structure of the precipitate isolated from the cement composites exposed in 0.5% citric acid.

As is seen from Fig. 3, the precipitate consists of the crystals of low-soluble calcium citrate and has a needle shape. This is an optimal shape for a crystal developing

Table 1. Results of analysis of filtrate (mg/L) after (five-day) exposure of cement stone with filler (size of ZR particles, 0.315 mm) in solutions of oxalic, tartaric, and citric acids (NA) ($n = 3$, $t_{p,f} = 4.3$, $p = 0.95$)

ω_{NA}, %	ω (ZR in the concrete), %	Ca^{2+}	Mg^{2+}	Fe^{3+}	Al^{3+}
Solutions of citric acid					
0.5	10	136.860 ± 0.004	14.771 ± 0.002	6.84 ± 0.11	73.1 ± 0.1
	30	179.35 ± 0.02	24.465 ± 0.001	7.40 ± 0.12	115.1 ± 0.1
0.1	10	114.99 ± 0.01	13.610 ± 0.004	14.37 ± 0.09	177.2 ± 0.1
	30	120.84 ± 0.01	11.20 ± 0.01	15.25 ± 0.12	190.4 ± 0.1
2.0	10	136.86 ± 0.02	14.77 ± 0.02	38.77 ± 0.10	802.7 ± 0.1
	30	333.873 ± 0.008	24.86 ± 0.01	42.09 ± 0.08	963.7 ± 0.1
Solutions of tartaric acid					
0.5	10	97.80 ± 0.07	5.322 ± 0.003	1.070 ± 0.001	2.73 ± 0.06
	30	115.452 ± 0.004	7.528 ± 0.007	1.195 ± 0.004	4.403 ± 0.002
0.1	10	276.431 ± 0.006	13.08 ± 0.07	2.859 ± 0.003	–
	30	417.178 ± 0.005	17.391 ± 0.002	2.68 ± 0.03	92.820 ± 0.044
2.0	10	259.793 ± 0.005	21.12 ± 0.01	7.04 ± 0.01	–
	30	417.178 ± 0.001	17.931 ± 0.001	6.99 ± 0.10	125.75 ± 0.003
Solutions of oxalic acid					
0.5	10	72.910 ± 0.004	2.754 ± 0.007	1.19 ± 0.01	53.836 ± 0.007
	30	18.57 ± 0.01	–	1.118 ± 0.004	204.060 ± 0.002
0.1	10	28.32 ± 0.02	–	1.39 ± 0.01	92.84 ± 0.01
	30	29.081 ± 0.005	–	1.18 ± 0.03	366.707 ± 0.004
2.0	10	0.253 ± 0.005	–	1.26 ± 0.01	142.18 ± 0.02
	30	0.589 ± 0.004	–	1.247 ± 0.006	358.78 ± 0.02

Table 2. Results of analysis of precipitate (for oxide content, %) obtained after (eight-day) exposure of cement stone with filler (size of ZR particles, 0.315 mm) in solutions of tartaric and citric acids (NA) according to data from energy-dispersive X-ray microanalysis

ω_{NA}, %	ω (ZR in the concrete), %	CaO	Al_2O_3	Fe_2O_3	SiO_2	K_2O	MgO
Precipitates after [ARC1] contact with solutions of tartaric acid							
0.5	10	66.91	0.55	3.11	1.31	0.62	–
	30	28.74	0.36	1.03	0.43	–	–
1.0	30	34.10	1.17	1.76	2.16	0.08	0.20
2.0	10	21.56	1.28	0.84	1.49	0.34	–
	30	27.99	0.45	1.21	1.18	–	–
Precipitates after contact with solutions of citric acid							
0.5	10	23.48	0.43	0.13	2.40	0.16	–
	30	29.85	0.40	0.19	1.89	0.10	0.12
2.0	10	24.49	0.49	0.29	4.78	0.14	–
	30	26.57	0.38	0.21	4.01	0.18	–

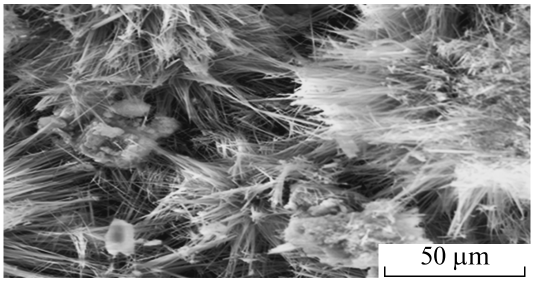

Fig. 3. Structure of precipitate obtained on scanning electron microscope at magnification ×1600.

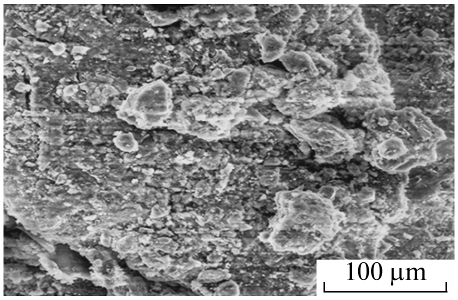

Fig. 4. The microstructure of cement not subjected to action of solutions of carboxylic acids (magnification ×800).

and growing in porous bodies and media. That is why the growth of the crystals of such a type in the pores of the cement composite creates strains in the inner structure and is the reason for the destruction of the cement.

After and further drying of the samples (cubes) of the cement composites in the 0.5, 1.0, and 2.0% solutions of oxalic, tartaric, and citric acids, they were subjected to strength tests using a destructive method. The results are presented in Table 3 depending on the nature of the contacting solution, molar fraction of the acid (HA) in it, degree of filling of the cement composites with the ZR, and the size of the particles of the ZR.

It is seen from Table 3 that composites exposed in the model solutions of oxalic acid possess the highest strength, while those soaked in the solutions of citric acid possess the lowest strength. During the analysis of the data presented in Table 3, it should also be noted that cement composites filled with ZR by 10% with the grain size of the filler of 0.315 and 0.63 mm possess a higher strength. With the increase in the degree of filling of the composites with the ZR to 30%, their strength decreases notably irrespective of the nature of the contacting solution. Apparently, this is associated with a decrease in the adhesion of the component in the system with the increase in the amount of argillaceous admixtures contained in ZR. When the content of ZR in the composite is high (30%), a sharp increase in the amount of the precipitate in the filtrate after exposing the samples in the solutions of tartaric and citric acids is also observed, which gives evidence of their growth in the processes of deterioration of the cement. Therefore, the content of the ZR during the production of the concrete should not exceed 10–20% of the mass of the dry cement mixture.

The experimental data show that the structure of the composite should be as homogeneous as possible in order to enhance the properties of the materials prepared from it. Figure 4 shows the image of a cement composite unaffected by solutions of carboxylic acids. The image is obtained on the Quanta 200i 3D FEI multi-purpose scanning electron microscope with an integrated focused ion beam system (at the magnification of ×800).

It is seen from Fig. 4 that the structure of this material was initially rather heterogeneous. While exposing such a composite in the aggressive media under study, the crystal nucleation takes place particularly on the elements of heterogeneities, which further creates internal strains and results in the deterioration of the structure of the concrete.

Table 3. Strength of cement composites filled with ZR after exposure [ARC2] in solutions of carboxylic acids

ω_{NA}, %	ω (ZR in the concrete), %	Size of ZR particles, mm	Strength, MPa
After contact with solutions of oxalic aci			
0.5	10	0.63	51.33
	20	0.63	50.44
	30	0.315	50.40
1.0	10	0.63	52.68
	20	0.63	50.85
2.0	10	0.63	51.95
	10	0.315	49.67
After contact with solutions of tartaric acid			
0.5	10	0.63	50.42
	10	0.315	48.83
1.0	10	0.63	47.28
	10	0.315	49.43
2.0	10	1.25	37.92
	10	0.63	39.62
After contact with solutions of citric acid			
0.5	10	0.63	43.16
	10	0.315	43.08
1.0	10	0.63	44.58
	10	0.315	44.76
	20	0.63	41.92
2.0	10	0.63	39.55
	10	0.315	45.80
	30	0.63	40.06

CONCLUSIONS

Therefore, we have shown based on the results of the study that alkali washing of calcium compounds from the cement takes place during the contact of cement composites with the solutions of carboxylic acids, which results in a change in the pH of the contacting solutions. The increase in the pH is most of all observed in the case of contact with solutions of citric acid and least of all with the solutions of oxalic acid. It is determined that large amounts of calcium compounds and smaller amounts of iron, aluminum, and magnesium compounds are contained in both solutions after the contact with the cement stone and precipitates crystallizing from these solutions. The rationalization for the processes taking place in the cement stone-model solution of carboxylic acid systems has been provided based on the modern analytical methods such as ion chromatography, atomic absorption spectroscopy, energy-dispersive X-ray microanalysis, and crystalline microchemical studies.

REFERENCES

1. Selyaev, V.P., Neverov, V.A., Kupriyashkina, L.I., Osipov, A.K., and Udina, O.A., in *Int. Sci. Conf. "Science, Technology, and Higher Education," Westwood, Canada, April 17, 2013*, 2013, vol. 2.
2. Selyaev, V.P., Osipov, A.K., Kupriyashkina, L.I., Volkova, S.N., and Epifanova, N.A., *Izv. VUZov, Stroit. Arkhit.*, 1999, no. 4, p. 36.
3. Selyaev, V.P., Kupriyashkina, L.I., Nugaeva, G.R., and Kozlov, P.S., *Izv. VUZov, Stroit. Arkhit.*, 2010, no. 6, p. 14.
4. Stroganov, V.F., Sagaev, E.V., and Potapova, M.I., *Izv. Kazan. Gos. Arkhit.-Stroit. Univ., Stroit. Mater. Izdeliya*, 2011, no. 4 (18), p. 274.
5. Korostelev, P.P., *Prigotovlenie rastvorov dlya khimiko-analiticheskikh rabot* (Preparation of Solutions for Chemical-Analytic Analysis), Moscow, 1984.
6. *GOST M-03-505-119-03. Metodika kolichestvennogo khimicheskogo analiza. Opredelenie metallov v pit'evoi, mineral'noi, prirodnoi, stochnoi vode i v atmosfernykh osadkakh atomno-absorbtsionnym metodom* (Quantitative Chemical Analysis: Determination of Metals in Drinking, Mineral, Natural, Waste Waters, and Atmospheric Precipitations by Atomic Absorption), 2003.
7. *Rukovodstvo pol'zovatelya personal'nym ionnym analizatorom Shimadzu PIA-1000* (Customer's Guide for Individual Ion Analyzer Shimadzu PIA-1000).
8. *Instruktsiya pol'zovatelya atomno-absorbtsionnym spektrometrom Shimadzu AA-7000* (Customer's Manual to Atomic Absorption Spectrometer Shimadzu AA-7000).
9. *PNDF 14,1:2:3:4.121-97. Metodika vypolneniya izmerenii pH v vodakh potentsiometricheskim metodom* (PNDF 14,1:2:3:4.121-97. Manual for Water pH Measurement by Potentiometer).
10. *Rukovodstvo pol'zovatelya k rastrovomu elektronnomu mikroskopu Quanta 200i 3D FEI* (Customer's Manual to Scanning Electronic Microscope Quanta 200i 3D FEI).
11. Rabinovich, V.A. and Khavin, Z.Ya., *Kratkii khimicheskii spravochnik* (Brief Chemical Handbook), Leningrad, 1978.

Translated by E. Boltukhina