

UDC 546.49+121 546.492

## Demercurization of Solid Wastes

L. M. LEVCHENKO, V. V. KOSENKO, A. A. GALITSKY, A. K. SAGIDULLIN and O. V. SHUVAEVA

*Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)**E-mail: luda@niic.nsc.ru*

### Abstract

Demercurization of solid mercury-containing wastes with the help of oxidizing agents and mercury-removing solution of calcium polysulphide were studied. The major regularities of mercury removal from luminophore (luminescent and compact lamps), granosan and soil were studied. It was shown that this method of mercury removal allows obtaining low-toxic wastes of the 4th class of danger.

**Key words:** demercurization processes, mercury-containing wastes, calcium polysulphide solution

### INTRODUCTION

Development of the technologies of demercurization of mercury-containing wastes is extremely urgent because mercury is a well known superecotoxicant. The problems of the prevention of pollution with mercury are to a high extent determined by the efficiency of technologies used for detoxication of mercury-containing wastes. In the world practice, the methods recognized as the most promising ones are those based on sorption processes, and those leading to the formation of wastes related to the 4th class of danger, or safe [1–10].

Various approaches and methods are used to develop demercurization technologies for processing solid wastes. For example, the methods of foreign researchers (MRT System, Sweden, or DYTEK, the USA) are based on the following major principles:

- Rejection of the use of high-temperature (thermal) and “wet” (hydrometallurgical) technologies, in order to exclude the formation of emissions and sewage that would enter the environment.

- Formation of as small as possible number of processing products, which decreases the probability of mercury scattering [11–19].

In this connection, the attention of researchers is presently attracted to the processes of demercurization of mercury-containing wastes (MCW) that go at room temperature using demercurization solutions that provide the transformation of mercury into poorly dissociating compounds. Among known demercurization agents [18–22], preferred are polysulphide solutions (of sodium, calcium) because ferric chloride, potassium permanganate, sodium thiosulphate and other solutions in use at present do not provide the complete transformation of mercury and a decrease in the level of air pollution with mercury to the MPC (0.0003 mg/m<sup>3</sup>). In addition, it was established that due to the instability of the formed compounds, an increase in the concentration of mercury vapour in the air to the initial level occurs within a definite time interval after demercurization (2–3 weeks) because of the formation of unstable compounds. For example, this occurs after demercurization of objects with the help of ozone or hydrogen peroxide: free mercury is released as a result of the decomposition of the reaction product which is the oxide of univalent mercury. It is noted that the high efficiency of demercurization is exhibited by the method allowing the transformation of mercury into mercury sulphide, the most stable and

almost insoluble compound of this element corresponding to its natural form [10, 18].

The goal of the present work was to study the processes of demercurization of mercury-containing wastes (luminophore of luminescent and compact lamps, granosan and soil) with the application of oxidizers and the demercurization solution of calcium polysulphide.

## EXPERIMENTAL

The luminophore of luminescent and compact lamps, granosan and soil were chosen as the objects of investigation.

The luminophore is a crystalline loose with admixture of crumbled glass containing mercury. This is the product of processing worked out luminescent lamps. The results of the anal-

TABLE 1

Composition of powdered luminophore of luminescent lamps (error of determination  $\leq 25\%$ ), mass %

Elements	Luminophore			Glass	
	of luminescent lamps	treated with $\text{HNO}_3$	Compact Electronix	Phoenix Light	of lamps
Aluminium	0.09	0.10	0.45	2.6	0.45
Barium	>10	>10	>4	>4	>4
Beryllium	<0.0004	<0.0004	0.0004	0.013	0.0005
Boron	0.002	0.002	0.35	0.20	0.30
Vanadium	0.004	<0.003	<0.003	<0.003	<0.003
Bismuth	<0.0004	<0.0004	0.002	0.0002	0.002
Gallium	<0.001	<0.001	<0.001	<0.001	<0.001
Hafnium	<0.001	<0.001	0.32	0.08	0.0006
Germanium	<0.0003	<0.0003	0.0006	<0.0003	0.0006
Iron	0.30	0.06	0.0008	0.06	0.06
Gold	<0.001	<0.001	<0.001	<0.001	<0.001
Yttrium	0.007	0.002	>0.3	>0.3	0.15
Cadmium	0.02	0.0003	0.0003	0.0005	0.0004
Calcium	7.7	2.3	>3	>3	>3
Cobalt	0.001	0.001	0.002	0.001	0.001
Silicon	>2	>2	>5	>5	>5
Lanthanum	<0.0003	<0.0003	0.0005	0.0007	<0.0002
Magnesium	1.0	1.0	0.3	>1	0.09
Manganese	0.10	0.004	0.002	0.01	0.003
Molybdenum	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Arsenic	0.02	0.03	0.13	0.06	0.03
Copper	0.005	0.001	0.003	0.001	0.004
Nickel	0.002	<0.0003	0.001	<0.0003	0.005
Tin	0.03	0.02	0.015	0.014	0.016
Palladium	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Platinum	<0.001	<0.001	<0.001	<0.001	<0.001
Rhodium	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Ruthenium	<0.0004	<0.0004	<0.0004	<0.0004	<0.0004
Lead	0.085	0.15	0.8	0.08	0.70
Silver	0.0005	0.0003	0.0003	0.0002	<0.0001
Antimony	0.18	0.020	0.04	0.005	0.04
Titanium	0.003	0.005	0.008	0.003	0.002
Chromium	0.001	0.001	0.001	0.0006	0.0006
Zinc	0.0065	0.0026	0.01	0.005	0.01

ysis of luminophore powder of luminescent and compact lamps are shown in Table 1. Characterization of the macro- and microelement composition of luminophore samples under investigation was performed by means of atomic emission spectrometry with the arc excitation of spectra (AES). Analyses were carried out with the PGS-2 spectrometer (Carl Zeiss Jena, Germany) with the diffraction grating as the dispersing element and the photodiode bar to record the spectra. A two-lens system of slit irradiation was used; the slit width was 20  $\mu\text{m}$ . The arc discharge current was 10 A, exposure was 18 s. Before analysis the electrodes were cleaned from surface contamination by means of preliminary annealing for 20 s at the current of 12 A. The solid samples to be analysed were ground in a mortar made of organic glass, then diluted with graphite powder containing sodium chloride as the amplifying additive at a level of 4 %. Sequential dilution of the sample 4, 8, 16, 32, 64 and 128 times was used during the preparation of the samples for analysis. This method of sample preparation for analysis allowed sequential increase in the degree of identity of the object under investigation and reference samples prepared from graphite powder with 4 % NaCl. The series of reference samples for plotting the calibration curve were prepared by sequential dilution of the concentrate of microelements with the basic mixture – graphite powder containing 4 % NaCl. The concentrate of microelements was prepared through serial deposition of aqueous solutions containing Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sb, Sn, Zn, on graphite powder, evaporation under the IR lamp under the conditions excluding contamination, and subsequent homogenization in the mortar made of organic glass. As a result, we obtained the unified series of reference samples with microelement concentrations within the range 0.014–33 mg/kg on the basis of graphite powder containing 4 % NaCl.

It follows from the data shown in Table 1 that the composition of luminophores of luminescent lamps is complicated and includes a mixture of barium, calcium silicates ( $\text{BaSiO}_4$ ,  $\text{CaSiO}_3$ ), additives of the pigment  $\text{Fe}_2\text{O}_3$  and activators manganese, lead, antimony, cadmium, cobalt, arsenic, tin, copper, nickel and rare

earths (yttrium). In the case of compact luminescent lamps Compact Electronix and Phoenix Light, the luminophore is represented by yttrium oxide, activated by europium, which was confirmed also by the X-ray phase analysis with Shimadzu XRD-7000 diffractometer. The crystal phase with the parameters of the cubic unit cell approximately equal to 10.6  $\text{\AA}$  was detected in the samples of all the compact luminescence lamps.

Treatment of the sample of luminophore powder with nitric acid caused the transformation of a part of metals into solution: iron, yttrium, calcium, manganese, copper, nickel, tin, lead, zinc. In this connection, it is necessary to keep in mind that the use of nitric acid solutions in the technology of MCW demercurization will require solving the problem of utilization of the solutions containing the listed metals.

Soil to be subjected to demercurization was a layer collected in the sites of storage and treatment of mercury-containing wastes. Granosan is a mixture containing 2 % ethylmercury chloride, a dye, mineral oil and filler. The latter was widely used in agriculture for seed treatment, and the problem of utilization of its reserve is still urgent. According to the XPA data, granosan chosen for investigation contains the phases of natural talc  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ , magnesium carbonate  $\text{MgCO}_3$  and an insignificant amount of the phase the weak reflections of which coincide with the most intense reflections of  $\text{HgCl}_2$ .

Mercury content in MCW was determined by means of atomic absorption spectrometry with the Yuliya analyser. Determination of mercury content in granosan (G1–G5 samples), luminophore (L1–L5), and soil (S1–S5) was carried out with five parallel weighted portions of 1 g. The weighted portions were multiply washed in turn with nitric acid and water, the volume of the solution was brought to 100 mL. For analysis, the solutions were diluted in the following manner: G1–G5 samples – 5000-fold (sequentially 1 mL in 100 mL, then 1 mL in 50 mL), L1–L5 samples – 2500-fold (sequentially 1 mL in 100 mL, then 2 mL in 50 mL). The results of the determination of mercury content in the objects under investigation and its concentration in washing water are shown

TABLE 2

Mercury content in luminophore (L1–L5), granosan (G1–G5), soil (S1–S5)

Samples	Diluted solution to be analysed, mg/L	Solution after washing the weighted portion, mg/L	Initial weighted portion, mg/g	Average, mg/g
L1	0.0024	6.11	0.61	0.57±0.03
L2	0.0023	5.85	0.58	
L3	0.0023	5.85	0.58	
L4	0.0022	5.50	0.55	
L5	0.0021	5.24	0.52	
G1	0.0079	39.27	3.93	4.00±0.42
G2	0.0073	36.48	3.65	
G3	0.0076	38.05	3.80	
G4	0.0078	38.92	3.89	
G5	0.0095	47.30	4.73	
S1	0.0069	38.27	3.83	3.94±0.40
S2	0.0073	36.48	3.65	
S3	0.0076	38.05	3.80	
S4	0.0058	36.92	3.69	
S5	0.0095	47.30	4.73	

in Table 2. It was demonstrated that mercury content in luminophore samples is 0.06–0.12 mass %, granosan 0.4 mass %, soil 0.039 mass %.

Mercury determination in compact luminescent lamps of the new generation was carried out with the used lamps having no signs of mechanical damage. The lamps were disassembled: the lamp cap, electronic board, plastic case were separated. The glass tube with the luminophore was fractured and ground to the state of crumbled glass in the desiccator under the layer of diluting solution 400 mL in volume (50 mL of concentrated HNO<sub>3</sub> + 0.2 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> per 1 L of water). The solution was poured into a volumetric flask 500 mL in volume. The crushed glass was washed two or three times more with small portions of the solution. The solution in the volumetric flask was brought up to the mark, then diluted by a factor of 1250 (sequentially 1 mL in 50 mL, then again 2 mL in 50 mL). The diluted solution was analysed for mercury content (Table 3). It was shown that mercury content in modern compact luminescent lamps varies within the range 0.014–0.07 mg/g.

For demercurization, we used the solution of calcium polysulphide with various additives of calcium oxide, calcium hypochlorite chloride Ca(Cl)OCl (active chlorine content 28 %)

and sodium hypochlorite NaClO (active chlorine content 4–7 %).

The solution of calcium polysulphide was obtained by mixing sulphur, lime and water at a ratio of 1.8 : 1 : 10 according to reaction  $\text{CaO} + \text{S} + \text{H}_2\text{O} \rightarrow \text{CaS}_n$  (1). The resulting mixture was boiled for 2 h (adding water to the constant volume). The solution was used after dilution (up to 50 times) but stored in the concentrated form because sulphur gets precipitated from the diluted solution as early as after 10 days. The solution of CaS<sub>n</sub> was analysed for sulphur and calcium content by means of photocolourimetry and atomic absorption. It should be noted that this demercurization agent is not volatile, not toxic, can be stored in any vessel, does not leave intensely coloured traces on the surface after application (unlike for ferric chloride or manganese compounds). In addition, its production can be arranged directly at the site where the process is performed.

## RESULTS AND DISCUSSION

From the viewpoint of ecological safety, not only the general mercury content in the sample under investigation is important but also the amount of labile mercury, that is, its soluble

TABLE 3

Mercury content in compact luminescent lamps

Lamps	Mass, g		Mercury content		
	of lamps	of crushed glass	Diluted solution, mg/L	Solution from washing crushed glass, mg/L	Crushed glass, mg
Phoenix Light 25W	106.54	44.06	0.0028	3.45	1.72
The same	84.34	38.48	0.0024	2.97	1.48
Compact Electronic 20W	107.32	37.04	0.0017	2.14	1.07
The same	105.8	35.87	0.0008	1.00	0.50
Compact Electronic 23W	109.62	52.19	0.0026	3.27	1.64
The same	103.13	47.75	0.0020	2.53	1.27
Compact Electronic 26W	112.67	55.88	0.0034	4.19	2.09
The same	112.9	55.47	0.0028	3.49	1.75
Svetlon 30W	102.34	42.38	0.0051	6.41	3.21
The same	102.44	38.46	0.0046	5.72	2.86
Happy Light 28W	73.07	29.47	0.0036	4.45	2.23
Kosmos SP 26W	117.88	55.5	0.0052	6.50	3.25

form easily washed with water. To determine this parameter, a weighted portion of 10 g was flooded with an aliquot of distilled water (25 mL), kept for 1 h, filtered, and then mercury content in solution was determined.

As one can see in the data shown in Table 4, in the case of granosan the treatment with calcium polysulphide solution immediately causes an order of magnitude decrease in the amount of mercury determined in washing solution, while such an effect is not observed for luminophore and soil. This is likely to be connected with the fact that mercury in granosan is present mainly in the ion form, while in luminophore mercury is in the metal state up to 95 %, according to the data of preliminary analysis. Soil can also contain a substan-

tial fraction of metal mercury. It is necessary to transform metal mercury into the ion form, that is, to perform oxidation process before treatment with calcium polysulphide solution. After testing several oxidizers, we chose bleaching powder as the most available, cheap and efficient reagent.

To determine the efficiency of luminophore demercuration with its preliminary oxidation, we performed experiments with large portions of the material (2 kg). The calculated amount of bleaching powder was added to the weighted portion of the luminophore (2012.5 g). The mixture was wetted with water to the homogeneous state and stored for 24 h. Then the mixture was flooded with 1 L of demercuration solution obtained by diluting concentrated  $\text{CaS}_n$  solution by a factor of 20. The pasty mass was applied on tray and dried in the exhaust box. Then samples of 10 g were taken from the dried material, washed with the aliquots (25 mL) of distilled water in which then the concentration of washed off mercury was determined (Table 5).

So, the addition of oxidizer causes a substantial increase in the efficiency of demercuration until the oxidizer is taken in large excess (approximately up to 10 %). The excess oxidizer starts to interact with the demercuration solution.

Additional experiments also showed that heating to 70 °C of the mixture of the lumino-

TABLE 4

Mercury concentration in the solutions of washing granosan treated with calcium polysulphide solution

Amount of $\text{S}^{2-}$ , mg-eq./g of granosan	Mercury content, $\mu\text{g/L}$
0	378±75
0.4	7.3±1.3
1.7	6.7±1.2
2.1	3.5±0.7
3.3	2.7±0.5
4.2	1.2±0.2
5.8	2.1±0.4

TABLE 5

Mercury concentration in the solution of one-time washing of luminophore after its oxidation and demercurization

Bleaching powder content, %	Mercury content, $\mu\text{g/L}$
0	4200 $\pm$ 800
5	0.75 $\pm$ 0.15
10	0.49 $\pm$ 0.09
20	225 $\pm$ 45
40	374 $\pm$ 70

phore with bleaching powder at the stage of oxidation decreases the consumption of bleaching powder (its optimal amount is at a level of 5%). However, such high-temperature processes would be of low efficiency in the case of industrial utilization of wastes.

Granosan containing  $\text{Hg}^{2+}$  does not require preliminary treatment with the oxidizer. With this material as example, we studied the major dependencies of mercury binding by the solutions of calcium polysulphide (reagents ratio, process time). Aliquots (25 mL) of calcium polysulphide solutions with different dilution degrees were added to weighted portions (60 g) of granosan. The mixture was mixed carefully until the state of uniformly wetted dense mass was achieved, kept for 2 h and washed with water (100 mL). Washing water was analysed for mercury content. Analysis results (see Table 4) show that the amount of sulphide sulphur necessary for efficient fixation of mercury is 4 mg/g of granosan.

The dependence of the degree of mercury binding on the time of exposure of granosan in mixture with calcium polysulphide solution was studied. Experimental conditions were similar to those described above. It follows from the data obtained (Table 6) that the dependence of the degree of demercurization process on time is rather weakly pronounced and is within the error limit of the instrument. A series of experiments was performed in which, in addition to calcium polysulphide solution, the addition of construction cement was used to harden the whole mass of granosan. Weighed portions of M-400 grade cement (6 or 10 g) were added to the weighted portions (30 g) of granosan, and then 20 mL of calcium polysulphide

TABLE 6

Mercury concentration in the solutions of granosan washing depending on its exposure in mixture with calcium polysulphide solution

Time, h	Mercury content, $\mu\text{g/L}$
0	94 $\pm$ 18
2	1.26 $\pm$ 0.25
24	1.23 $\pm$ 0.24
96	1.18 $\pm$ 0.24
336	1.26 $\pm$ 0.25

solutions with different dilution degree were added. A viscous mass was obtained; it turned into concrete after storage for 3 days. Mercury content in washing water that passed through the concrete sample (Fig. 1) did not exceed the MPC (0.0005 mg/L). Coloured (blue) solutions were formed during demercurization of granosan powder with calcium polysulphide solution, which brought complications into mercury determination. However, by adding cement we succeeded in obtaining transparent washing solutions and thus the accuracy of mercury determination in solution was increased. In addition, we studied the effect of cement additive on the degree of mercury fixation. To estimate the amount of mercury in the gas phase above the sample under study, we built



Fig. 1. View of cemented granosan sample.

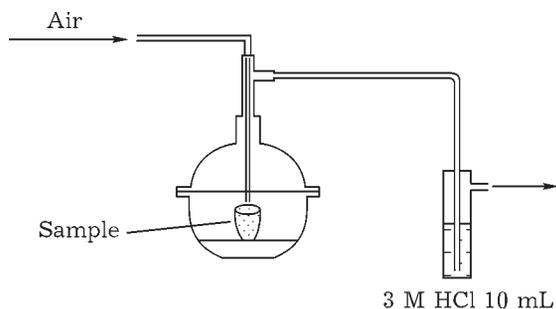


Fig. 2. Scheme of the set-up for the determination of mercury content in the gas phase above the sample.

a set-up (Fig. 2). Air flow rate was 1 L/min. The outgoing mercury-containing gas was trapped in 10 mL of a 3 M HCl solution. Experiment lasted for 30 min for each sample; the volume of passed air was 30 L. After blowing, the sample was subjected to single washing with water, then the washing solution was analysed. The results of mercury determination in the solutions of gas trapping and in the solutions of one-time washing the samples are shown in Table 7.

So, the studied dependencies of the changes of mercury concentration in washing water of cemented granosan show that the addition of cement additive noticeably decreases the

TABLE 7

Mercury concentration in the solutions of washing and blowing off granosan depending on the amount of introduced sulphide sulphur and cement

Amount of S <sup>2-</sup> , mg-eq./g of granosan	Cement content, %	C <sub>Hg</sub> , µg/L	
		after one-time washing	in gas trapping solution
0	0	378±75	–
0	20	254±50	1350±270
3.3	0	36±7.0	–
3.3	20	2.7±0.5	8.1±1.6
3.3	30	2.4±0.4	n/d
8.4	0	3.3±0.6	–
8.4	20	2.5±0.5	6.0±1.2
8.4	30	2.5±0.5	n/d
15.3	20	2.2±0.4	3.3±0.6
15.3	30	1.3±0.2	n/d
30.7	20	2.4±0.4	7.5±1.5
61.3	20	1.5±0.3	10.8±2.2

Note. n/d – not determined.

amount of washable mercury. It should be also noted that the formation of mercury wastes in compact blocks simplifies the problem of their transportation to the utilization site.

## CONCLUSION

On the basis of the data of X-ray phase and atomic emission analyses, it was established that the composition of luminophores of luminescent lamps is complicated and includes a mixture of barium, calcium silicates (BaSiO<sub>4</sub>, CaSiO<sub>3</sub> with the addition of pigment Fe<sub>2</sub>O<sub>3</sub> and activators manganese, lead, antimony, cadmium, cobalt, arsenic, tin, copper, nickel and rare earths (yttrium). In the case of compact luminescent lamps of Compact Electronix and Phoenix Light, the luminophore is represented by yttrium oxide activated with europium.

Mercury content, determined by means of atomic absorption spectrometry with the help of the Yuliya analyser, is 0.057 mass % in the luminophore of luminescence lamps; for compact luminescence lamps it varies within the range 0.0014–0.0074 mass % depending on the manufacturer.

It was shown that demercurization of luminophore of luminescent and compact lamps with the help of oxidizers (5–10 %) leads to the formation of mercury sulphide. In the case of demercurization of granosan and soil, the formation of mercury sulphide takes place in the interaction with the solution of calcium polysulphide.

## REFERENCES

- 1 Davydova S. L., Tarasov V. I., Tyazhelye Metally kak Supertoksikanty XXI veka, Izd-vo Ros. Un-ta Druzhby Narodov, Moscow, 2002.
- 2 Isidorov V. A., Vvedeniye v Khimicheskuyu Ekotoksikologiyu, Khimizdat, St. Petersburg, 1999.
- 3 Natsionalny Standart RF GOST R 52105–2003. Resursosberezheniye. Obrashcheniye s Otkhodami. Klassifikatsiya i Metody Pererabotki Rtut'soderzhashchikh Otkhodov. Osnovnye Polozheniya.
- 4 Bespamyatov G. P., Krotov Yu. A., Predelno Dopustimye Kontsentratsii Khimicheskikh Veshchestv v Okruzhayushchey Srede, Khimiya, Leningrad, 1985.
- 5 RU Pat. No. 2264856, 2005.
- 6 Shavinskiy B. M., Levchenko L. M., Mitkin V. N., *Chem. Sustain. Dev.*, 14, 2 (2006) 181.  
URL: <http://www.sibran.ru/English/csde.htm>
- 7 Shavinskiy B. M., Levchenko L. M., Mitkin V. N., *Chem. Sustain. Dev.*, 16, 4 (2008) 449.

- URL: <http://www.sibran.ru/English/csde.htm>
- 8 Levchenko L. M., Mitkin V. N., Shavinskiy B. M., Trudy Kontserna "Nanoindustriya", Yanus-K, Moscow, 2008, pp. 115–126.
- 9 Kosenko V. V., Levchenko L. M., Galitskiy A. A., XII Nauch.-Prakt. Konf. "Khimiya – XXI Vek: Novye Tekhnologii, Novye Produkty", Kemerovo, 2009, pp. 162–163.
- 10 RU Pat. No. 240054, 2010.
- 11 JP Pat. No. 2009291734, 2009.
- 12 JP Pat. No. 2010042346, 2010.
- 13 RU Pat. No. 2171304, 2001.
- 14 RU Pat. No. 2148662, 2000.
- 15 RU Pat. No. 22022640, 2001.
- 16 Gyibadullin N. Sh., Shirobokova A. V., Khalturin V. G., *Usp ekhi Sovrem. Estestvoznaniya*, 5 (2007) 30.  
URL: <http://www.rae.ru>
- 17 RU Pat. No. 2083709, 1997.
- 18 15 RU Pat. No. 2175664, 2001.
- 19 Levchenko L. M., Kosenko V. V., Galitskiy A. A., Badmaeva Zh. O., Vseros. Nauch.-Prakt Soveshch. "Litiy Rossii: Mineralno-Syryevye Resursy, Innovatsionnye Tekhnologii, Ekologicheskaya Bezopasnost" (Proceedings), Izd-vo SO RAN, Novosibirsk, 2011, pp. 179–183.
- 20 Kosorukova N. V., Yanin E. P., *Svetotekhnika*, 3 (2002) 25.
- 21 RU Pat. No. 2240337, 2004.
- 22 Makarchenko G. V., Kosorukova N. V., *Ekol. Prom-sti Rossii*, 1 (2003) 44.