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The research of $(\text{NH}_4)_2\text{BeF}_4$ solution purification effectiveness

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Abstract

The research work topicality is based on necessity of beryllium production from fluorine containing raw materials technology optimization, beryllium losses minimization and environmental impact decrease by beryllium and materials based on beryllium production. The goal of research is identification of beryllium containing solutions produced in the result of beryllium concentrate fluorineammonium processing purification possibility (clarification of iron, aluminum, calcium and silicon) and conditions provided maximum impurity removal from solution, which do not cause beryllium hydrolysis.

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Keywords: fluorineammonium technology; fluorite-phenacite-bertrandite concentrate; ammonium hydrogenfluoride; ammonium tetrafluoroberyllate; precipitation; hydrolysis

1. Introduction

From year to year world industry requirement of beryllium is increasing. The amount of extractive beryllium (in conversion to metal) has increased by 65 % from 2001 to 2015 [1,2]. The general world beryllium consumption in 2015 was about 400 ton in conversion to metal [3,4]. The beryllium cost depending on purity is volatile between 300-1500 \$/kg [3]. Due to high cost beryllium is used in spheres where its use is critical and use of alternate metals (titanium, graphite, aluminum, magnesium etc.) results in a valid decrease of technical-operational characteristics. Such critical spheres in industry are copper-beryllium alloys, metallic beryllium and beryllium ceramics productions.

Currently 72 % of world beryllium consumption is accounted for by copper-beryllium alloys (Be content is 0.1-2 %); 20 % of consumable beryllium is used as pure metal for creation of metal matrixes consisting of beryllium by 50 %; 8 % of beryllium is used for beryllium ceramics [5]. Beryllium is used for telecommunication and telephone

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equipment production (12 %), medical equipment production (5 %), transport construction (14 %), aerospace industry (32 %), energetics, oil, gas industry (12 %), defense and military industry (2 %), security systems production (3 %), and consumer electronics (20 %) [6].

Beryllium is extracted from beryl, bertrandite and bertrandite-phenacite concentrates [7]. For beryllium production extreme monopoly degree is indicative. Full cycle factories which process natural beryllium raw materials and technology-related waste processing to ready-made beryllium production are situated only in three countries: USA, Kazakhstan and China [8-10]. There are no such factories in Russian Federation. There is only one factory in Saratov oblast («Bazalt» Federal State Unitary Enterprise (FSUE)) which processes ready-made products – beryllium oxide, metallic beryllium and beryllium alloys and produces special beryllium objects (items). This factory is included in State Atomic Energy Corporation «Rosatom» [11]. At the same time there are unique beryllium deposits in the territory of Russia: Ermakovskoe, Malyshevskoe, and Zavitinskoe. Ermakovskoe deposit represents the biggest economic interest for capital providers (BeO average grade is 0.85 %). The capacity of this deposit is 1,394 thousand tons of commercial ore, which mainly consists of fluorite-phenacite-bertrandite metasomatites [12, 13].

The processing of fluorite-phenacite-bertrandite concentrate (FPBC) using classic sulfuric acidic scheme is constrained because of following factors [7]:

1. To destroy the crystal lattice of refractory phenacite before sulfuric acidic extraction it is necessary to add preliminary high temperature (1700 °C) procedure of concentrate and flux materials (soda, limestone) syntexis. It causes the conversion prime cost increasing. The cost increases because of expenses for flux materials and extra amount of sulfuric acid, which is needed to neutralize forming alkali fusion.
2. Fluoride-ion from fluorite mineral after syntexis and sulfuric acidic extraction of fusion goes into water phase together with beryllium. On the stage of Be(OH)₂ precipitation fluoride-ion blocks full extraction of beryllium into solid phase. It causes beryllium loss. The environmental impact increases because mother liquors after Be(OH)₂ filtration go to sludge depository. All facts mentioned above negatively influence prime cost of beryllium containing materials sulfuric acidic processing.

2. Technology description

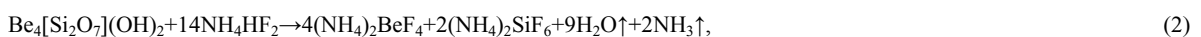
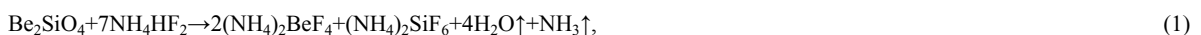
So to process Ermakovskoe deposit ore another technology is needed. Such technology must provide conversion low prime cost by virtue of raw material activation preliminary operations elimination, absence of liquid wastes, possibility of water flows cycling and leaching agent regeneration. For reasons of beryllium production prime cost decrease fluorineammonium method of beryllium containing raw materials processing have been developed.

To research and test the fluorineammonium method of beryllium containing raw materials processing the FPBC have been used. FPBC contains as macro components beryllium, iron, aluminum, calcium, silicon and fluorine (Table 1).

Table 1. Fluorite-phenacite-bertrandite concentrate composition.

Substance	BeO	SiO ₂	CaF ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
Content, %	5.0	36.8	20.7	11.4	24.0	2.1

FPBC is mixed with ammonium hydrogenfluoride (NH₄HF₂). The mixture is sintered at 200 °C. Fluorite (CaF₂) does not react with NH₄HF₂. The hydrofluorination of FPBC components in ammonium hydrogenfluoride fusion runs with ammonium fluorometallates formation [14-21]:





To separate soluble beryllium constituent from fluorine containing impurities compounds the fluorinated concentrate is dissolved in water. The solubility of ammonium tetrafluoroberyllate ((NH₄)₂BeF₄) at 25 °C is 323 g/l of solution [22], ammonium hexafluorosilicate ((NH₄)₂SiF₆) – 210 g/l [23], ammonium hexafluoroaluminate ((NH₄)₃AlF₆) – 10.4 g/l [24], ammonium hexafluoroferrate (III) ((NH₄)₃FeF₆) – 4.3 g/l [25], calcium fluoride is insoluble [23]. Besides, ammonium tetrafluoroberyllate only (NH₄)₂SiF₆ moves in water phase (Table 2). The water amount added for fluorinated concentrate dissolving has been calculated by mass correlation S:L = 1:4, where “S” is solid phase (fluorinated concentrate), “L” is water for dissolving. Ammonium hydrogenfluoride concentration in forming solution is 81.2 g/l.

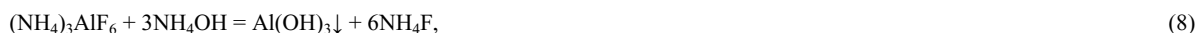
Table 2. Impurities content in (NH₄)₂BeF₄ solution, mg/l.

Be	Fe	Al	Ca	Si
5150.00	228.50	24.50	32.12	12950.00

3. Experimental

The goal of research is identification of ammonium tetrafluoroberyllate solution effective purification by 25 % ammonia solution possibility and identification of conditions which provide maximum impurity removal (silicon, iron, aluminum and calcium) and do not cause precipitation of beryllium. The need in purification is based on requirements to chemical composition of beryllium production – beryllium oxide and metallic beryllium mark B-1 [26-27].

To remove impurities gone in water phase, the precipitation stage has been offered to get in. The precipitation of impurities is realized because of complex fluorine containing anions hydrolysis at high pH levels by adding strong alkali, in this case 25 % water ammonia solution. Fluoroberyllate anion hydrolysis does not happen by ammonia solution adding (stability constant is $2.27 \cdot 10^{15}$) [22]. Impurities precipitation process is described by following reactions [28-29]:



Ammonium fluoroberyllate solution purified by this way should be used to produce crystalline (NH₄)₂BeF₄ and beryllium fluoride (BeF₂), which in its turn is the starting compound for metallic beryllium production or beryllium hydroxide. To evaluate effectiveness of impurities removal from beryllium containing solution the experiments series of beryllium and impurities concentration changing depending on pH level changing over the range 5.0 to 11.0 has been realized. Precipitation purification has been done at 25 °C and with constant stirring. The doses of ammonia solution have been added in the way to reach accurately each pH unit. Forming pulp has been mixed for 10 minutes and filtered. Before reaching pH unit 8.0 the precipitation was not observed (Fig. 1).

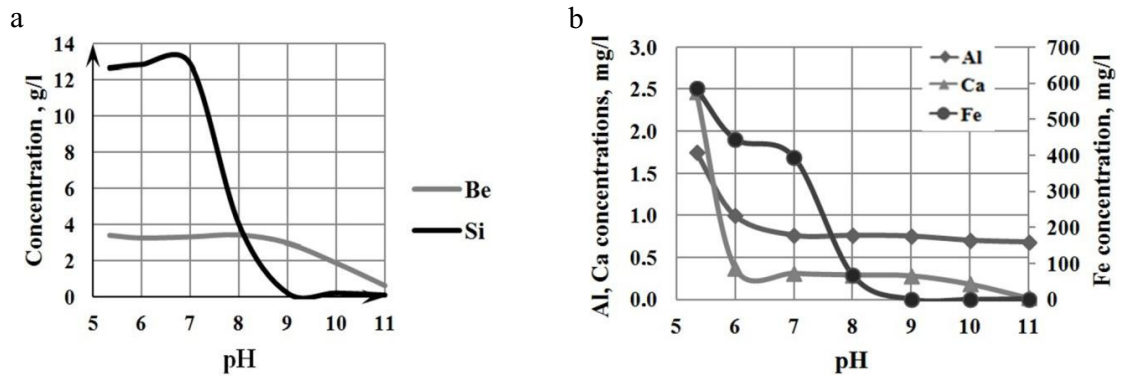


Fig. 1. (a) Be и Si concentrations changing depending on pH level changing; (b) metal impurities concentrations changing depending on pH level changing.

It has been identified that more complete impurities removal takes place before tetrafluoroberyllate-ion hydrolysis over the range pH = 8.0-9.0 (Fig. 2).

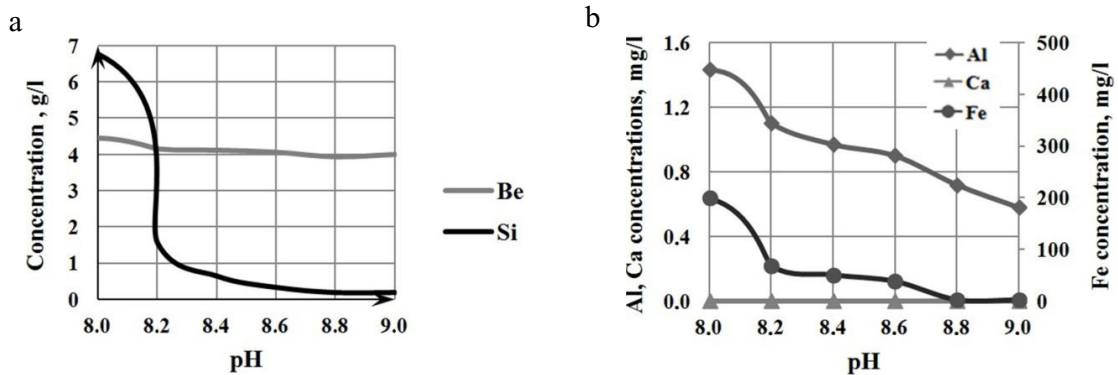


Fig. 2.(a) Be and Si concentrations changing over the range pH = 8.0-9.0; (b) Fe, Al and Ca concentrations changing over the range pH = 8.0-9.0.

The most complete purification of beryllium containing solution takes place in the range of pH = 8.8-9.0. At the same time, 20 % of beryllium removes from the prime solution with impurities. As the result of solution purification, 98 % of iron, 64 % of aluminum, 100 % calcium, and 97 % silicon have been removed.

To decrease beryllium losses and increase beryllium containing solution purification effectiveness the influence of following factors over purification process has been researched:

1. introduction of elutriation of impurities hydroxides precipitate;
2. increase of impurities precipitation temperature.

The process of impurities precipitation (crystalline structure formation) is endothermal. Increase of system temperature must intensify precipitate particles formation. The elutriation of forming precipitates with distilled water must remove occluded beryllium from amorphous precipitate volume; precipitate is presented by silicon hydroxides mixture [30]. As the result of elutriation the concentration of ammonia and ammonium fluoride decreases in impurity hydroxides volume. It increases beryllium fluorine containing salts dissociation and solubility.

3.1. Method of precipitating purification

Solution initial volume for each experiment was 100 ml. Solution was heated to needed temperature (25, 40, 65 °C) and pH level was registered. The solution color was registered. Needed amount of 25 % ammonium hydroxide solution was added to heated solution to define pH = 7.00; 8.00; 9.00. The solution color was registered again. When at mentioned pH levels precipitation realized forming pulp was filtered. Forming precipitate was repulped in 50 ml of water, and then pulp was filtered again. After liquid smooth mirror on precipitate surface formed 50 ml of distilled water was added. Washed precipitate was dried at 200 °C and calcined at 900 °C. Produced precipitates masses and washing solution volumes were registered (Table 3).

Table 3. Experimental data.

Characteristic	Precipitation temperature, °C		
	25	40	65
Initial pH level	4.90	4.83	3.88
Solution color	Light cyan	Light cyan	Light cyan
Volume of 25 % NH ₄ OH to pH = 7, ml	44.5	46.5	31.0
Solution color (pH = 7)	Cyan	Cyan	Cyan
Solution temperature (pH = 7), °C	42.0	59.4	69.7
Volume of 25 % NH ₄ OH to pH = 8, ml	19.5	18.5	19.0
Solution temperature (pH = 8), °C	36.0	58.3	61.1
Precipitate mass (pH = 8), g	2.835	2.145	3.290
Washing solution volume, ml	124	114	82
Volume of 25 % NH ₄ OH to pH = 9, ml	41.5	45.0	50.0
Solution temperature (pH = 9), °C	18.0	19.0	24.0
Precipitate mass (pH = 9), g	0.940	1.080	0.275
Washing solution volume, ml	117	110	103
Purified solution volume, ml	173	185	203

When temperature changed after pH level increase the correction of experiment temperature was realized by heating on electric hot plate or cooling by locating testing solution in can with cold water.

To identify washing and purified solutions composition the aliquots (1 ml) were collected from each phase.

Purified solution produced at 65 °C got cold and digested during 12 hours, in the result the white precipitate formed. Calcined residue mass was 0.020 g.

Table 4. Elements hydrolysis degrees at pH = 9,00, %.

T = 25 °C				
Be	Fe	Al	Ca	Si
0.46	94.48	58.49	100.00	91.97
T = 40 °C				
Be	Fe	Al	Ca	Si
0.74	89.59	31.63	100.00	85.45
T = 65 °C				
Be	Fe	Al	Ca	Si
1.42	98.30	54.57	100.00	91.38

In the result of precipitation at 25 °C about 80 % of beryllium primary amount stayed in purified solution. In the result of elutriation of precipitate produced at pH = 8.00 about 12 % of beryllium moved to liquid phase. About 0.24 % of beryllium at pH = 8.00 moved to precipitate. In the result of elutriation of precipitate produced at pH = 9.00 about 4 % of beryllium moved to liquid phase. About 0.22 % of beryllium at pH = 9.00 moved to precipitate (Table 4). In the result of precipitation the purification degree of solution from iron is 98 %, aluminum – 64 %, calcium – 100 %, silicon – 97 % (Fig. 3).

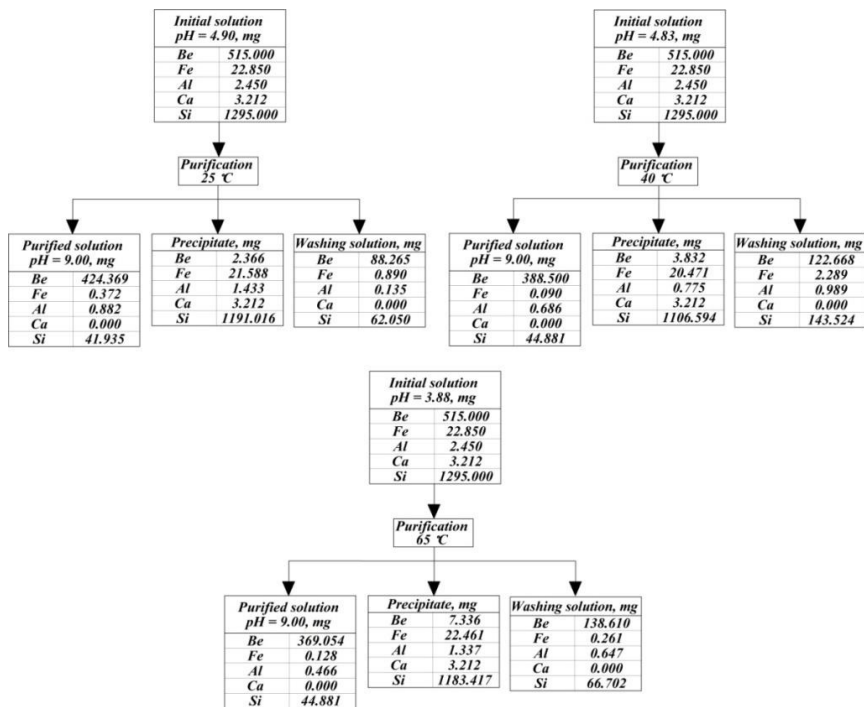


Fig. 3. Mass balance of purification operations at 25, 40, 65 °C

In the result of precipitation at 40 °C, about 75 % of beryllium primary amount stayed in purified solution. In the result of elutriation of precipitate produced at pH = 8.00 about 18 % of beryllium moved to liquid phase. About 0.32 % of beryllium at pH = 8.00 moved to precipitate. In the result of elutriation of precipitate produced at pH = 9.00 about 6 % of beryllium moved to liquid phase. About 0.42 % of beryllium at pH = 9.00 moved to precipitate (Table 4). In the result of precipitation the purification degree of solution from iron is 99.6 %, aluminum – 72 %, calcium – 100 %, silicon – 97 % (Fig. 3).

In the result of precipitation at 65 °C, about 72 % of beryllium primary amount stayed in purified solution. In the result of elutriation of precipitate produced at pH = 8.00, about 25 % of beryllium moved to liquid phase. About 1.31 % of beryllium at pH = 8.00 moved to precipitate. In the result of elutriation of precipitate produced at pH = 9.00, about 2 % of beryllium moved to liquid phase. About 0.11 % of beryllium at pH = 9.00 moved to precipitate (Table 4). In the result of precipitation, the purification degree of solution from iron is 99.4 %, aluminum – 81 %, calcium – 100 %, silicon – 96 % (Fig. 3).

Precipitates produced at pH = 8.0-9.0 have the form of mixture of silicon, iron, aluminum, calcium, and beryllium hydroxides. If the extraneous purification is realized (for example, washing with hydrochloric acid), the synthesis of extra-pure hydrated silica could become possible. The extra-pure silica is used to produce «white carbon» – silicon dioxide.

4. Conclusion

1. Iron, aluminum, and silicon hydrolysis most completely passes during conditioning by 25 % ammonia solution in the range $\text{pH} = 8.8-9.0$ in testing system. The use of ammonia solution to purify ammonium tetrafluoroberyllate solution does not provide complete removal of iron, aluminum and silicon.
2. The temperature increase to 65 °C triples the beryllium hydrolysis degree: from 0.46 % at 25 °C to 1.42 % at 65 °C. Large beryllium amount (~ 27 %) is absorbed by forming impurities hydroxides precipitate but it is not exposed by hydrolysis. Beryllium losses are minimized by forming precipitates elutriation and use produced washing solution in FPBC processing.
3. The dependence of impurities precipitation degrees from temperature is indefinite. At 25 °C the maximum purification from silicon ions takes place (91.97 %) and aluminum (58.49 %). At 65 °C the most complete removal of iron takes place – 98.30 %. Calcium at pH level of 9.00 is not found in testing solutions.

References

- [1] LLC «Infomain» Researching group». Survey of beryllium market in Russia, CIS and the world. Moscow, 2014. pp. 8-16.
- [2] S.M. Kimball, U.S. Geological Survey, Reston, Virginia, 2015, pp. 28-29.
- [3] Beryllium Science & Technology Association (BeST), Production Statistics, Available at: <http://beryllium.eu/about-beryllium-and-beryllium-alloys/facts-and-figures/production-statistics/> (accessed 18.01.2016).
- [4] European Commission, Report on critical raw materials for the EU, 2014, pp. 28-36.
- [5] Beryllium Science & Technology Association (BeST), Critical Applications of Beryllium, Available at: <http://beryllium.eu/about-beryllium-and-beryllium-alloys/critical-applications-of-beryllium/> (accessed 18.01.2016).
- [6] Beryllium Science & Technology Association (BeST), Uses of Beryllium, Available at: <http://beryllium.eu/about-beryllium-and-beryllium-alloys/uses-and-applications-of-beryllium/> (accessed 18.01.2016).
- [7] Samoylov V.I., Borsuk A.N., Methods of phenacite, bertrandite and beryl co-processing in beryllium hydrometallurgy, Media-Alliance, Ust-Kamenogorsk, 2006, pp. 12-20.
- [8] Beryllium Science & Technology Association (BeST), Industry Profile, Available at: <http://beryllium.eu/about-beryllium-and-beryllium-alloys/industry-profile/> (accessed 18.01.2016).
- [9] Nine-monthly report 2003 year of Close Corporation «Kazatoprom» National Nuclear Company», Almaty, 2003, pp. 9-10.
- [10] Prospectus of bond issue «Ulbian Metallurgical Factory» JSC, Ust-Kamenogorsk, 2005, pp. 24-25.
- [11] «Bazalt» FSUE, Available at: <http://www.sarbazalt.ru/> (accessed 18.01.2016).
- [12] Methodological recommendations on application of the Classification of deposits and forecast resources of solid minerals. Beryllium ores. Approved by the decree of the Ministry of Natural Resources of the Russian Federation from 05.06.2007 № 37-p, Moscow, 2007, pp. 5-10.
- [13] «Eastern Siberian Metals» Corporation, Mining sector, Ernakovskoe deposit, Available at: <http://www.mbc-corp.com/activity/gorsector/ermak/index.wbp> (accessed 18.01.2016).
- [14] D.D. Thorat, B.M. Tripathi, D. Sathiyamoorthy, Extraction of beryllium from Indian beryl by ammonium hydrofluoride, Hydrometallurgy. 109 (2011) 18-22.
- [15] E.E. Zaki, Z.H. Ismail, J.A. Daoud, H.F. Aly, Extraction equilibrium of beryllium and aluminium and recovery of beryllium from Egyptian beryl solution using CYANEX 921, Hydrometallurgy. 80 (2005) 221-231.
- [16] A.A. Andreev, A.N. Dyachenko, R.I. Kraydenko, Fluorination of beryllium concentrates with ammonium fluorides, Russian Journal of Applied Chemistry. 81 (2008) 178-182.
- [17] V.S. Rimkevich, A.A. Pushkin, A.A. Malovitskii, Yu.N. Dem'yanova, I.V. Girenko, Fluoride processing of non-bauxite ores, Russian Journal of Applied Chemistry. 82 (2009) 6-11.
- [18] V.A. Kovzalenko, N.M.-K. Sadykov, R.A. Abdulvalieyv, V.S. Rimkevich, A combination technology for high-silica raw material treatment by means of fluoride method, Obogashchenie Rud. 5 (2015) 54-59.
- [19] L.N. Kurilenko, N.M. Laptash, E.B. Merkulov, V.Yu. Gluschenko, About fluorination of silicon containing minerals by ammonium hydrodifluoride, El. J. «Researched in Russia». 130/021011 (2002) 1465-1471.
- [20] N.M. Laptash, I.G. Maslennikova, L.N. Kurilenko, N.M. Mischenko, Fluorination of ilmenite by ammonium hydrodifluoride. New ammonium oxofluorotitanate, Russian Journal of Inorganic Chemistry. 46 (2001) 33-39.
- [21] A.A. Udovenko, N.M. Laptash, I.G. Maslennikova, Orientation disorder in ammonium elpasolites. Crystal structures of $(\text{NH}_4)_3\text{AlF}_6$, $(\text{NH}_4)_3\text{TiOF}_5$ and $(\text{NH}_4)_3\text{FeF}_6$, Journal Fluorine Chemistry. 124 (2003) 5-15.
- [22] G.F. Silina, Yu.I. Zarembo, L.E. Bertina. Beryllium. Chemical technology and metallurgy, Atomizdat, Moscow, 1960, pp. 52-54.
- [23] I.G. Ryss, Chemistry of fluorine and its inorganic compounds, Goshimizdat, Moscow, 1956, pp. 365-700.
- [24] A. Seidell, Solubilities of inorganic and metal organic compounds, third ed., V.I, D. Van Nostrand Company, New York, 1940, pp. 90.
- [25] T. Watanabe, M. Hoshino, K. Uchino, Y. Nakazato, A new acid and iron recovery process in stainless steel annealing and pickling line, Kawasaki Steel Technical Report (Tokyo), № 14, 1986, pp. 72-82.
- [26] V.L. Balkevich, Technical ceramics: Manual for graduate students, Stroyizdat, Moscow, 1984, pp. 128.
- [27] «Ulbian Metallurgical Factory» JSC, Production, Beryllium, Available at: <http://www.ulba.kz/ru/production21.htm> (accessed 04.02.2016).

- [28] Ripan R., Chetyanu I. Inorganic Chemistry. Chemistry of metals, V. 2, Mir, Moscow, 1972, pp. 519-520.
- [29] V.S. Rimkevich, A.A. Pushkin, I.V. Girenko, Development of hydrochemical method of thermal engineering factories ash industrial wastes enrichment, *Fundamental research*. 2 (2015) 5156-5160.
- [30] A.V. Novosyolova, L.R. Batcanova, Beryllium analytical chemistry, Science, Moscow, 1966, pp. 146-147.