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Obtaining Bismuth and Its High-Purity Compounds

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Abstract

The process of metal bismuth dissolution in nitric acid was studied, and a comparison was made over environmentally friendly methods of obtaining bismuth nitrate solutions by the preliminary oxidation of bismuth, as well as by its dissolution in the presence of urea or ammonium nitrate. It has been shown that the dissolution of bismuth in the presence of ammonium nitrate at a molar ratio of ammonium nitrate to bismuth equal to 1.5–3.5 and a temperature of 70 ± 5 °C allows eliminating the release of nitrogen oxides into the gas phase and obtaining a solution with a high concentration of bismuth. The feasibility of two-stage hydrolytic processing of a bismuth-containing nitrate solution in order to purify bismuth from impurity metals is shown. The first stage is the aqueous hydrolysis of a bismuth-containing solution by adding a bismuth nitrate solution to water heated to 60 °C at a volume ratio of water to bismuth-containing solution 9 : 1, and the second stage is additional precipitation of bismuth from the mother solution after aqueous hydrolysis by adding ammonium carbonate solution to reach pH 1 at a temperature of 55 ± 5 °C. Based on the research carried out, ecologically safe technologies have been developed for the production of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ and bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, as well as specially pure bismuth(III) oxide. As a result of the reduction of bismuth(III) oxide in molten sodium hydroxide containing sulphur at a temperature of 500 °C and at a ratio of bismuth(III) oxide/sodium hydroxide/sulphur equal to 1: 1.31: 0.20, high-purity metallic bismuth was obtained.

Keywords: technical-grade bismuth, nitrate solutions, hydrolytic purification, bismuth compounds, high purity, bismuth oxohydroxonitrate, bismuth nitrate pentahydrate, bismuth(III) oxide, metallic bismuth

INTRODUCTION

Bismuth relates to rare metals, and its average content in the Earth's crust is at a level of $(9 \cdot 10^{-7}) - (2 \cdot 10^{-5})$ % according to different estimates. The amount of bismuth spent annually in the world is 21 thousand t [1], and it follows from the diagram shown in the review that bismuth is used in the form of various compounds, %: oxide – 28.6, nitrates – 11.4, metal – 20.0, salicylate – 17.1, oxochloride – 15.7, and other – 7.2 %. The data on the planned production of bismuth and its com-

pounds for the years 2023–2032 are reported in [2]. The world market of bismuth was estimated in 2023 as 464.17 mln US dollars, and it is expected to reach 759.17 mln US dollars by 2032 at the mean annual growth rate of 5.8 %.

Bismuth and its compounds are widely used in technology and in medicine [3, 4]. The initial raw material is metal bismuth of Bi 1 grade, obtained by pyrometallurgical processing of lead, copper, tin, molybdenum-tungsten concentrates. At the state of concentrate processing, a lead-bismuth alloy is formed as the intermediate product. It is

processed by electrolysis in a hydrofluorosilicic electrolyte or from the melt of its salts to obtain the Bi 1 grade metal [5, 6]. The major impurity metals in the Bi 1 grade bismuth are lead, silver and copper, while bismuth content is not less than 98.0 %.

Bismuth compounds are usually obtained by dissolving the granules of metal bismuth in nitric acid. About 50 % of nitric acid is transformed into toxic nitrogen oxides. The hydrolytic purification of bismuth nitrate solutions is carried out by adding a solution of alkaline reagent, while the initial compounds for obtaining high-purity bismuth compounds are usually bismuth oxide, basic or neutral bismuth nitrates. In turn, it has been proposed to obtain high-purity metal bismuth from the technical-grade metal using the amalgamation process by dissolving crude bismuth in mercury under the layer of diluted perchloric acid and isolating bismuth from the amalgam by electrolysis [7]. Crude bismuth is refined using different methods: chlorination and reduction of the resulting bismuth trichloride by hydrogen [8], chlorination in the flow of tetrachloromethane pyrolysis products at 950–1200 °C, followed by bismuth condensation at 450–500 °C [9], chlorination of bismuth melt during bubbling a mixture of tetrachloromethane and inert gas at 550–600 °C. To remove chlorine-containing compounds from bismuth melt, it is additionally blown with a mixture of ethyl alcohol and inert gas [10].

A hydrometallurgical method has been proposed for metal bismuth refining, based on metal dissolution in nitric acid, precipitation of the major part of silver by hydrochloric acid, removal of residual silver and other precious metals by cementation of the nitric solution with metal bismuth, hydrolysis of the purified solution, drying, annealing, and reduction of the basic salt [11]. As a result of the application of this purification scheme, the metal was obtained containing the following impurities at a level of, wt%: silver $3 \cdot 10^{-6}$, lead $3 \cdot 10^{-3}$, antimony $1 \cdot 10^{-4}$, iron $<1 \cdot 10^{-3}$, copper $1 \cdot 10^{-3}$, (selenium + tellurium + arsenic) $1 \cdot 10^{-3}$, manganese $5 \cdot 10^{-3}$, cobalt $5 \cdot 10^{-3}$, zinc $1 \cdot 10^{-3}$.

In the present work, the data are summarised on environmentally friendly dissolution of bismuth in nitric acid, efficient purification of the resulting nitric acid solution from metal impurities, and the methods of obtaining high-purity bismuth and its compounds by processing these solutions.

EXPERIMENTAL

The reagents used in the work included nitric acid, sodium hydroxide, aqueous ammonia, ammonium hydrocarbonate, ammonium nitrate of chemically pure reagent grade, elemental sulphur of specially pure 15-3 grade, and metal bismuth of Bi 1 grade (KazZinc PLC, Kazakhstan) containing, wt%: bismuth 98.1, lead 1.2, zinc $1.4 \cdot 10^{-4}$, iron $2.8 \cdot 10^{-3}$, antimony $8.2 \cdot 10^{-4}$, copper $1.2 \cdot 10^{-3}$, silver $1.2 \cdot 10^{-1}$, arsenic $<1 \cdot 10^{-4}$, cadmium $1 \cdot 10^{-5}$ and tellurium $<1 \cdot 10^{-4}$. Under laboratory conditions, metal oxidation was carried out in a cup made of stainless steel, 1 L in volume, with bismuth mass per load 200 g, bismuth oxide 30 g, the melt was mixed at 350 °C for 30 min, then temperature was increased to 600 °C, and mixing went on for 90 min at this temperature point. The degree of bismuth transformation into the oxide in this process is not less than 97 %. Initial bismuth-containing solutions were obtained either by the dissolution of technical-grade bismuth oxide in nitric acid or by the dissolution of 1.0 kg of metal bismuth granules in 2.2 L of nitric acid in the concentration of 7.15 mol/L, containing ammonium nitrate in the amount of 940 g. Dissolution was carried out in a porcelain beaker 3.0 L in volume at a temperature of 70 ± 5 °C under permanent mixing.

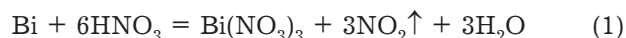
The X-ray diffraction (XRD) analysis of the products was carried out with a powder diffractometer D8 Advance (Bruker, Germany) using CuK_α -radiation within the angle range (4–70)° over 2θ with a step of 0.02° and signal integration time 35 s per point. Phase identification was carried out using the powder database ICDD PDF2 (2011). The electron images of samples were taken with a scanning electron microscope TM 1000 (Hitachi, Japan). Nitrogen oxide content was determined by gas chromatography with an Agilent 7000B GC/MS instrument (Agilent Technology, USA). Bismuth concentration in solution and its content in the solid reaction products were measured by titration with complexone III solution, adding xylenol orange as an indicator. Metal bismuth and bismuth compounds obtained in experiments (oxide Bi_2O_3 , oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ and nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) were preliminarily dissolved in nitric acid in the concentration of 7 mol/L. The content of micro-amounts of bismuth and admixture metals was determined by atomic absorption with the AA 280FS spectrophotometer (Varian, Australia) and by atomic

emission spectrometry with inductively coupled plasma using Agilent 8800 instrument (Japan). The concentration of free nitric acid in solutions was measured by acid-base titration after preliminary masking bismuth with complexone III. The specific surface of samples was measured by the thermal desorption of argon with the internal reference at the liquid nitrogen temperature. The bulk density was determined according to GOST 19440-94 [12]. The acidity of solutions was measured with a pH meter OP-264/1 (Radex, Hungary) with a glass electrode.

RESULTS AND DISCUSSION

The chemical mechanism of bismuth dissolution in nitric acid

Bismuth compounds are usually obtained from the Bi 1 grade metal by dissolving its granules in nitric acid in the concentration of 7–9 mol/L, followed by the hydrolytic purification of bismuth at the stage of precipitation in the form of basic nitrate [3, 13]. About 50 % of nitric acid is transformed in this process into toxic nitrogen oxides according to reaction equation [13, 14]:



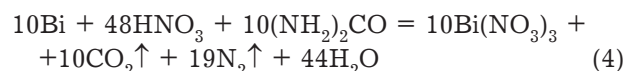
To prevent the formation of nitrogen oxides evolving during bismuth dissolution, it is proposed to employ its preliminary oxidation to oxide [15], and to add carbamide at the stage of bismuth dissolution [14]. The use of bismuth oxide as the starting compound allows eliminating the evolution of nitrogen oxides because now dissolution proceeds according to the equation:



It has been proposed in [15] to oxidise metal bismuth by mixing the melt with the single-charged metal in the amount of 200 g at 350–600 °C for 2 h. The oxidation of metal bismuth with atmospheric oxygen can be represented by the equation:



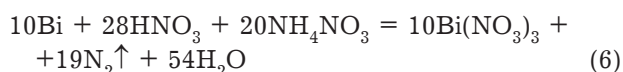
Bismuth dissolution in nitric acid in the presence of carbamide proceeds as



It is known [16] that the interaction of nitrogen oxides with the solutions of ammonium nitrate in nitric acid proceeds with the defixation of bound nitrogen according to reaction



In this regard, the possibility arises to dissolve metal bismuth in nitric acid, avoiding the evolution of toxic nitrogen oxides, the process will follow the reaction:



Obtaining bismuth solutions in nitric acid

During the dissolution of metal bismuth or its oxide in nitric acid, the dependence of bismuth concentration in solution on the initial concentration of the acid passes through a maximum at the concentration of 8 mol/L [3]. With an increase in acid concentration, in the descending region of the dependence, bismuth precipitates as the nitrate pentahydrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$). For this reason, it is proposed to dissolve metal bismuth in nitric acid in the concentration of 7.44 mol/L to obtain the solution containing bismuth in the concentration of 250 g/L [13]. The data on the dissolution of metal bismuth in nitric acid, as well as in the presence of carbamide or ammonium nitrate, and the data on bismuth oxide dissolution are presented in Table 1. One can see that bismuth reacts with nitric acid to form solutions containing 370–410 g/L bismuth, but in the case the percentage of nitrogen oxides formed in the gas phase is 66–69 % (see Table 1).

After bismuth dissolution in the presence of 5 % carbamide, bismuth concentration in solution is only 282 g/L, and the concentration of nitrogen oxides in the gas phase does not exceed 0.01 %. In this case, non-dissolved residue is composed of bismuth granules and bismuth oxohydroxonitrate [$\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$]. The interaction of metal bismuth with nitric acid in the presence of ammonium nitrate at the molar ratio of ammonium nitrate to metal bismuth equal to 1.5–3.5 allows one to avoid the evolution of nitrogen oxides into the gas phase and to obtain solutions containing bismuth in the concentration of 415–447 g/L and free nitric acid 0.6–1.0 mol/L (see Table 1). The solutions obtained after hydrolytic processing of bismuth solutions in nitric acid can be used as the source of ammonium nitrate.

In the case of the dissolution of technical-grade bismuth oxide obtained by bismuth oxidation with atmospheric oxygen, bismuth concentration in solution is 267 g/L, and the concentration of nitrogen oxides in the gas phase is less than 0.01 %.

TABLE 1

Dissolution of Bi 1 grade metal bismuth and bismuth(III) oxide in nitric acid (14.3 mol/L) at 70±5 °C for 4 h

Experiment	Initial experimental parameters						Results of experiment				
	V_{H_2O} , mL	V_{HNO_3} , mL	HNO_3 in, mol/L	Bi, g	NH_4NO_3 , g	NH_4NO_3 /Bi, mol/mol	NO_2 , %	V , mL	Bi, g/L	HNO_3 eq, mol/L	R , %
1	130	70	5.0	70	–	–	–	185	238	0.83	64.1
2	115	85	6.1	70	–	–	48.8	183	329	0.85	87.7
3	100	100	7.15	80	–	–	66.0	183	372	0.92	86.7
4	85	115	8.2	90	–	–	69.2	182	413	1.04	85.1
5	100	100	7.15	90 ^a	–	–	<0.01	194	267	0.6	75.4
6	100	100	7.15	80 ^b	–	–	<0.01	190	282	0.98	68.3
7	100	100	7.15	90	25	0.74	2.8	186	397	0.85	83.6
8	100	100	7.15	90	50	1.48	0.02	199	413	0.62	93.1
9	100	100	7.15	90	70	2.07	0.01	205	415	0.62	96.4
10	100	100	7.15	90	100	2.96	<0.01	215	447	0.6	98.0
11	100	100	7.15	90	120	3.55	<0.01	220	441	0.6	98.8

Notes. 1 V is solution volume; HNO_3 eq is the equilibrium concentration of nitric acid; R is the degree of bismuth recovery into solution. 2 Dash – not added.

^a Bismuth oxide (Bi_2O_3) was dissolved.

^b Metal bismuth was dissolved in the presence of 4 g of carbamide.

Processing the solutions in nitric acid to obtain oxohydroxonitrate with the composition $[Bi_6O_5(OH)_3](NO_3)_5 \cdot 3H_2O$

As a result of the dissolution of metal bismuth granules (1 kg) in nitric acid in the presence of ammonium nitrate, the solution (S1) containing 435 g/L bismuth, 5.3 g/L lead and 0.60 mol/L free nitric acid is formed. It has been demonstrated previously [3] that the most efficient purification of bismuth from admixture metals is possible by the hydrolysis of bismuth-containing solutions in nitric acid as a result of adding water at the process temperature not lower than 50 °C. In the case of bismuth precipitation from the solutions in nitric acid after dilution with water at 20, 60 and 90 °C, the precipitation degree passes through a maximum, but complete precipitation of bismuth cannot be achieved even in the case of 200-fold (pH 1.7) and higher dilution of the solutions [3]. In addition, in the case of precipitation at 20 °C, bismuth purification from impurity metals is ineffective because bismuth remains in the form of $[Bi_6O_4(OH)_4](NO_3)_6 \cdot 4H_2O$ and is composed of the oriented aggregates of flat prismatic crystals united in packs with weak contacts between the basal planes. The latter fact brings complications into the purification of precipitate from the mother solution containing impurity metals. At the process temperature of 90 °C, the degree of bismuth precipitation in the form of bismuth oxohydroxonitrate $[Bi_6O_4(OH)_4](NO_3)_6 \cdot H_2O$ decreases

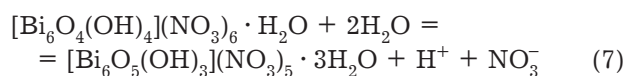
es. In this regard, it is reasonable to carry out the hydrolysis of S1 at a temperature of 60±3 °C and ten-fold dilution of the solution with distilled water. Then the precipitate is washed with nitric acid solution (0.1 mol/L) at 60 °C and twice with distilled water. The degree of bismuth recovery into the precipitate is ~80 % [17].

It should be noted that the degree of bismuth recovery into the precipitate is 97.9 % as a result of S1 neutralisation with the aqueous solution of ammonium hydroxide to pH 1, but with the addition of an alkaline reagent into the system, bismuth oxohydroxonitrate starts to sorb impurity metals, which causes a substantial decrease in product purity. For this reason, it is desirable to process the bismuth-containing solution in nitric acid in two stages. At the first stage, the aqueous hydrolysis of S1 is carried out, and the second stage involves the additional precipitation of bismuth from the mother solution by adding the solution of ammonium carbonate to pH 1 at 55±5 °C. The sequential hydrolysis of S1 with water and with ammonium carbonate solution to pH 1 allows efficient separation of bismuth from impurity metals to obtain high-purity bismuth oxohydroxonitrate.

The additional precipitation of bismuth from the mother solution and washing solutions at pH 3 is carried out by adding ammonium carbonate solution in the concentration 2.5 mol/L. Impurity metals were also precipitated by ammonium

carbonate at pH 8. Subsequent recycling of the bismuth-containing precipitate and ammonium nitrate solution to the stage of metal bismuth dissolution allows complete utilisation of bismuth and ammonium nitrate solution in the production of high-purity bismuth compounds.

Efficient purification of bismuth from metal impurities is due to the fact that in the case of high concentration in solution within pH 0–3 bismuth is present in the form of nanosized polynuclear complex $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$. Hydrolysis at a temperature above 50 °C causes bismuth precipitation in the form of well-crystallised oxohydroxonitrate with the composition $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$. Such impurity metals as lead, zinc, iron, copper, silver, cadmium are well soluble in 0.01–0.1 mol/L nitric acid solutions and remain in the mother solution. In addition, washing with water causes recrystallisation of this compound with the formation of oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ according to reaction



This causes additional purification of the precipitate from impurity metals captured during precipitation.

Solution S1 in the amount of 2.25 L with bismuth concentration 435 g/L was processed by adding it upon mixing in 20.0 L of distilled water heated preliminarily to 70 °C (the volume ratio of water to S1 was 9 : 1) and mixing the pulp for 30 min. The precipitate was washed once with 6.0 L of nitric acid solution with the concentration 0.1 mol/L at 60 °C and twice with 6.0 L of distilled water. Then the precipitate was dried on a pan made of stainless steel at 100 °C for 4 h. The product obtained by processing was 1.09 kg of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (according to ICDD PDF2 No. 70-1226). The results of chemical analysis are shown in Table 2. The direct recovery of bismuth into the product from metal bismuth is 80.1 %. The specific surface area of the resulting bismuth oxohydroxonitrate was 0.58 m²/g, and its bulk density was 1.55 g/cm³.

The mother solution after aqueous hydrolysis contains bismuth at a level of 8.2 g/L. To precipitate bismuth from this solution, the aqueous solution of ammonium carbonate in the concentration of 2.5 mol/L was added to pH 1 at 55 °C, mixing was carried out for 30 min, and then the mixture was settled for 2 h. The precipitate was washed once with 0.8 L of a 0.1 mol/L nitric acid solution at 60 °C and twice with 0.8 L of distilled water.

The washed precipitate of bismuth oxohydroxonitrate was dried at 100 °C for 4 h. Bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ in the amount of 228 g was obtained, the results of chemical analysis showed that the product meets the requirements of TS 2624-272-05785359-99 for chemically pure grade (see Table 2). The direct recovery of bismuth from metal bismuth into the product with the formation of two products (bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$) of chemically pure grade is 96.7 %.

After processing metal bismuth with the formation of bismuth oxohydroxonitrate, the total volume of mother solution and washing water is 38.2 L, and bismuth concentration in solution is 0.85 g/L. Bismuth was recovered by almost complete precipitation from this solution to the residual concentration 0.015 g/L (by adding ammonium carbonate solution to pH 3). The solution was separated from the precipitate by decanting, and the precipitate was directed to the stage of metal bismuth dissolution. Decanted liquid was used to precipitate lead, silver, copper, bismuth by adding ammonium carbonate solution to pH 8. The precipitate containing impurity metals was separated from the solution by filtering. After filtering, the solution containing, mg/L: bismuth 0.4, lead 3.2, silver 0.15, copper 0.05 and ammonium nitrate 58.5 g/L was directed to the stage of metal bismuth dissolution.

Obtaining bismuth nitrate pentahydrate

Bismuth nitrate pentahydrate $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is usually obtained from metal bismuth by dissolving it in 7–8 mol/L nitric acid. The solution contains bismuth 380–420 g/L, free nitric acid 1.0–1.5 mol/L, and the density of this solution is 1.55–1.60 g/cm³. The resulting solution is evaporated at 65–70 °C to the density of 1.9 g/cm³ (bismuth concentration in solution 620 g/L), cooled, and the crystallised product is dried at 40–60 °C [13, 18]. Metal dissolution in nitric acid proceeds according to equation (1). As mentioned above, the major disadvantage of this method is the release of toxic nitrogen oxides into the atmosphere at the stage of obtaining bismuth-containing solution, and the formation of nitric acid vapour during evaporation. From the viewpoint of environmental safety, it is more reasonable to obtain bismuth nitrate without evaporation according to the reaction of bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with the concentrated solutions of nitric acid.

TABLE 2

Results of the chemical analysis of bismuth nitrate samples

Parameter	Component content in the products, wt%				
	Bismuth oxohydroxonitrate [Bi ₆ O ₅ (OH) ₃](NO ₃) ₅ · 3H ₂ O			Bismuth nitrate pentahydrate Bi(NO ₃) ₃ · 5H ₂ O	
	1	2	3	4	5
Bismuth oxide	79–82	80.2	80.1	–	–
Major component	–	–	–	≥99.0	99.2
Lead	≤5 · 10 ^{–3}	<5 · 10 ^{–6}	5 · 10 ^{–3}	≤3 · 10 ^{–4}	<1 · 10 ^{–5}
Zinc	–	<1 · 10 ^{–5}	<4 · 10 ^{–5}	≤5 · 10 ^{–4}	<4 · 10 ^{–5}
Iron	≤5 · 10 ^{–4}	<1 · 10 ^{–5}	5 · 10 ^{–4}	≤3 · 10 ^{–4}	<5 · 10 ^{–5}
Antimony	–	<5 · 10 ^{–6}	<5 · 10 ^{–5}	–	–
Copper	≤6 · 10 ^{–4}	<1 · 10 ^{–5}	5 · 10 ^{–4}	≤3 · 10 ^{–4}	<5 · 10 ^{–5}
Silver	≤1 · 10 ^{–3}	<1 · 10 ^{–5}	8 · 10 ^{–4}	–	–
Arsenic	–	<1 · 10 ^{–5}	<5 · 10 ^{–6}	–	–
Cadmium	–	<1 · 10 ^{–6}	<1 · 10 ^{–6}	–	–
Tellurium	–	<5 · 10 ^{–6}	<5 · 10 ^{–6}	–	–
Calcium	≤3 · 10 ^{–4}	3 · 10 ^{–4}	3 · 10 ^{–4}	≤5 · 10 ^{–4}	<1 · 10 ^{–4}
Magnesium	≤5 · 10 ^{–4}	<4 · 10 ^{–4}	4 · 10 ^{–4}	≤5 · 10 ^{–4}	<5 · 10 ^{–5}
Sodium	≤5 · 10 ^{–3}	<1 · 10 ^{–4}	<1 · 10 ^{–4}	≤5 · 10 ^{–4}	<1 · 10 ^{–4}
Chlorides	≤5 · 10 ^{–3}	<1 · 10 ^{–3}	<1 · 10 ^{–3}	≤1 · 10 ^{–3}	<1 · 10 ^{–3}
Barium	–	–	–	≤3 · 10 ^{–4}	<1 · 10 ^{–4}
Vanadium	–	–	–	≤3 · 10 ^{–4}	<1 · 10 ^{–6}
Tungsten	–	–	–	≤1 · 10 ^{–4}	<1 · 10 ^{–4}
Cobalt	–	–	–	≤3 · 10 ^{–4}	<2 · 10 ^{–5}
Manganese	–	–	–	≤3 · 10 ^{–4}	<5 · 10 ^{–6}
Molybdenum	–	–	–	≤1 · 10 ^{–4}	<4 · 10 ^{–5}
Nickel	–	–	–	≤3 · 10 ^{–4}	<1 · 10 ^{–5}
Titanium	–	–	–	≤3 · 10 ^{–4}	<3 · 10 ^{–5}
Chromium	–	–	–	≤3 · 10 ^{–4}	<1 · 10 ^{–5}

Notes. 1. Bismuth oxohydroxonitrate: 1 – according to TS 2624-272-05785359-99, chemically pure grade; 2 – product was obtained by hydrolysis of bismuth-containing nitric acid solution by water; 3 – product was obtained by hydrolysis of bismuth-containing nitric acid solution with the addition of ammonium carbonate solution to pH 1. 2. Bismuth nitrate pentahydrate: 4 – according to TS 6-09-2230-77, specially pure 13-3 grade; 5 – product of [Bi₆O₄(OH)₄](NO₃)₆ · H₂O treatment with nitric acid. 3. Dash – no data.

The process of obtaining Bi(NO₃)₃ · 5H₂O from oxohydroxonitrate [Bi₆O₄(OH)₄](NO₃)₆ · H₂O was carried out as follows. Nitric acid in the amount of 100 L in the concentration of 13.9 mol/L was poured in a container made of corrosion-resistant steel, equipped with a mechanical mixer, then bismuth oxohydroxonitrate in the amount of 100 kg was added gradually during mixing, and the reaction was carried out for 1 h. The reaction mixture was self-heated to 40±5 °C, which promoted a complete transition of initial oxohydroxonitrate into bismuth nitrate. After cooling to 20 °C, the mother solution was collected with the help of vacuum, and humid crystals were transferred to the centrifuge. After centrifuging, the crystals were dried at 55±5 °C. The product with the composition Bi(NO₃)₃ · 5H₂O (ICDD PDF2

No. 44-314) was obtained. According to the data of chemical analysis (see Table 2), the product corresponds to a specially pure 13-3 reagent grade according to TS 6-09-2230-77.

Concentrated nitric acid was added to the mother solution with bismuth concentration 1 g/L, and the resulting solution was used for subsequent treatment of bismuth oxohydroxonitrate [Bi₆O₄(OH)₄](NO₃)₆ · H₂O. The direct recovery of bismuth into the final product is 85.2 %.

Obtaining bismuth(III) oxide

Bismuth precipitates from nitric acid solutions at the process temperature 60±3 °C and pH 1 in the form of well crystallised oxohydroxonitrate [Bi₆O₄(OH)₄](NO₃)₆ · H₂O. Its diffraction patterns

contain clearly pronounced maximums: $d/n = 7.55$; 3.78; 3.29; 2.63; 2.18; 1.73 Å. The composition of this substance was studied in [19]. According to electron microscopic data (Fig. 1, *a*), the substance is composed of aggregated short prismatic crystals with the largest size in the basal plane 1–5 µm, 1–3 µm thick. At the stage of precipitate washing with a 0.1 mol/L nitric acid solution at 60 °C it retains its composition, while after double washing of the precipitate with distilled water it is transformed as a result of hydrolysis completely into oxohydroxonitrate $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$. The structure of this compound was studied in [20]. According to electron microscopic data, the product is composed of elongated flat prismatic crystals 10–50 µm in size in the basal plane, 1–5 µm thick (see Fig. 1, *b*). The monoclinic modification of bismuth oxide was obtained by annealing bismuth oxohydroxonitrate at 620 ± 20 °C (ICDD PDF2 No. 14-699). The particles of bismuth oxide

are aggregates of fused grains 10–30 µm in size (see Fig. 1, *c*). The size of grains forming the aggregates is 2–6 µm. They are characterised by smoothed edges and angles. The regions of grain coalescence alternating with the cavities of complicated configuration, several ten micrometres in size.

Results of the chemical analysis of bismuth(III) oxide are shown in Table 3. One can see that the product corresponds to the requirements of TS 6-091853-77 for the specially pure 13-3 grade. The specific surface area of bismuth(III) oxide is 0.52 m²/g, and its bulk density is 1.90 g/cm³.

To obtain fine crystalline bismuth(III) oxide and eliminate the release of nitrogen oxides into the gas phase at the stage of annealing bismuth oxohydroxonitrate, the version of its preliminary transformation into basic carbonate by treating with ammonium carbonate solution at the molar ratio of ammonium carbonate to basic bismuth nitrate equal

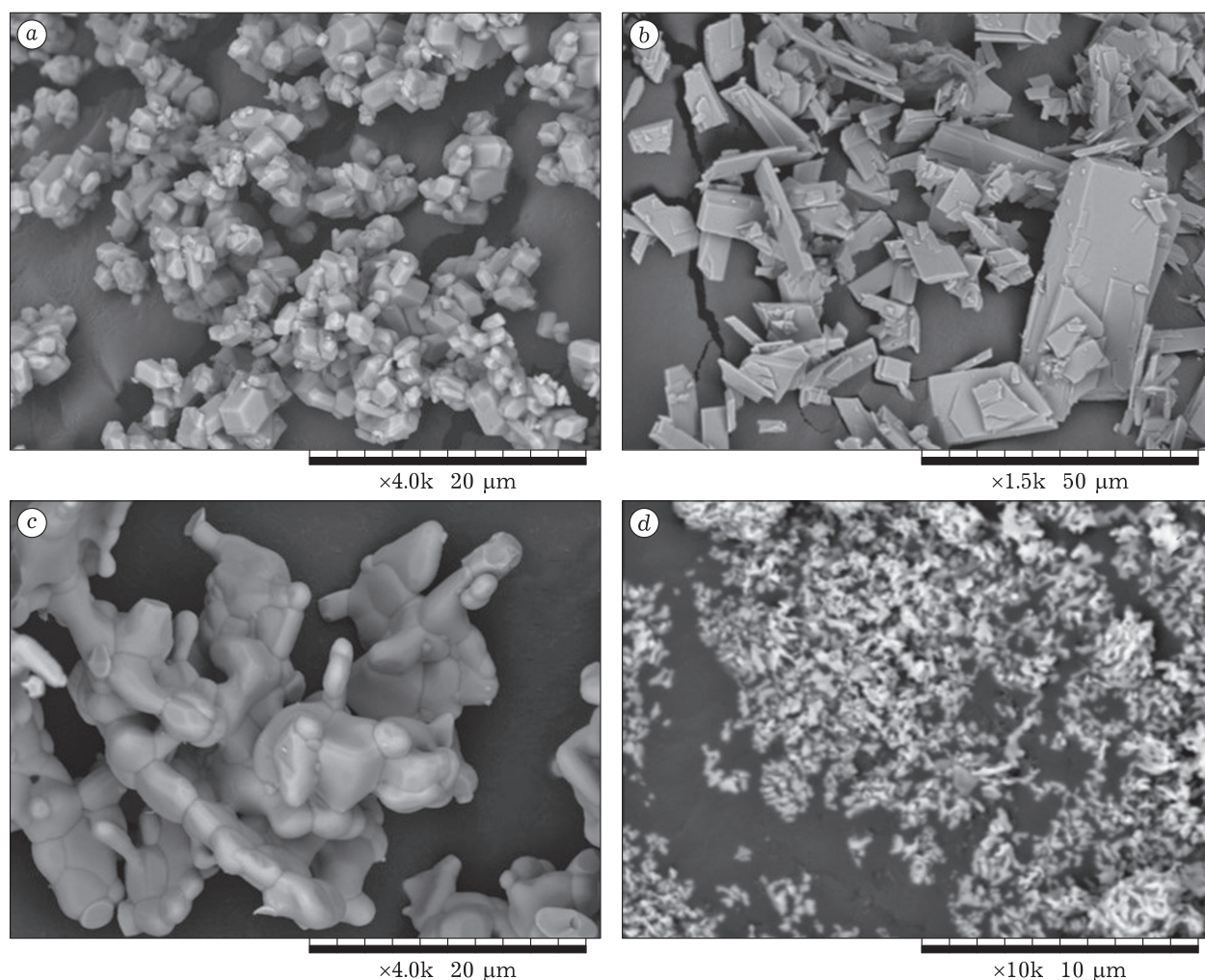


Fig. 1. SEM images of bismuth oxohydroxonitrate samples: $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ (*a*); $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (*b*); Bi_2O_3 oxide samples obtained by the thermal decomposition of $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ (*c*) and $(\text{BiO})_2\text{CO}_3$ (*d*).

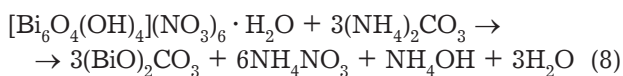
TABLE 3

Results of the chemical analysis of bismuth(III) oxide samples

Parameter	Content, wt%			
	1	2	3	4
Major component	≥99.5	99.6	≥99.5	99.6
Nitrogen	≤5 · 10 ⁻³	<5 · 10 ⁻³	≤5 · 10 ⁻³	<5 · 10 ⁻³
Barium	≤3 · 10 ⁻⁴	<3 · 10 ⁻⁴	—	—
Vanadium	≤3 · 10 ⁻⁴	<1 · 10 ⁻⁶	—	—
Tungsten	≤1 · 10 ⁻⁴	<1 · 10 ⁻⁴	—	—
Iron	≤5 · 10 ⁻⁴	<1 · 10 ⁻⁵	≤1.5 · 10 ⁻³	1 · 10 ⁻⁴
Calcium	≤1 · 10 ⁻³	<1 · 10 ⁻³	≤1 · 10 ⁻³	<1 · 10 ⁻³
Cobalt	≤3 · 10 ⁻⁴	<3 · 10 ⁻⁴	—	—
Magnesium	≤1 · 10 ⁻³	<5 · 10 ⁻⁴	≤1 · 10 ⁻³	<5 · 10 ⁻⁵
Manganese	≤3 · 10 ⁻⁴	<2 · 10 ⁻⁵	—	—
Copper	≤3 · 10 ⁻⁴	<1 · 10 ⁻⁵	≤1 · 10 ⁻³	2 · 10 ⁻⁴
Molybdenum	≤1 · 10 ⁻⁴	<1 · 10 ⁻⁴	—	—
Sodium	≤1 · 10 ⁻³	<1 · 10 ⁻³	≤1 · 10 ⁻³	<1 · 10 ⁻³
Nickel	≤3 · 10 ⁻⁴	<1 · 10 ⁻⁵	—	—
Lead	≤5 · 10 ⁻⁴	<5 · 10 ⁻⁶	≤5 · 10 ⁻³	8 · 10 ⁻⁴
Sulphates	≤5 · 10 ⁻³	<5 · 10 ⁻³	≤5 · 10 ⁻³	<5 · 10 ⁻³
Titanium	≤3 · 10 ⁻⁴	<3 · 10 ⁻⁴	—	—
Chlorides	≤1 · 10 ⁻³	<1 · 10 ⁻³	≤1 · 10 ⁻³	<1 · 10 ⁻³
Chromium	≤3 · 10 ⁻⁴	<3 · 10 ⁻⁵	—	—
Zinc	≤5 · 10 ⁻⁴	<1 · 10 ⁻⁵	—	—
Silver	—	<1 · 10 ⁻⁵	—	—

Notes. 1. Bismuth(III) oxide samples: 1 – according to TS 6-09-1853-77, specially pure 13-3 grade; 2 – product of $[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$ annealing at 620 ± 20 °C; 3 – according to GOST 10216-75, chemically pure grade; 4 – product of $(\text{BiO})_2\text{CO}_3$ annealing at 380 ± 20 °C. 2. Dash – no data.

to 0.55 was considered. As a result of treating bismuth oxohydroxonitrate $[\text{Bi}_6\text{O}_4(\text{OH})_4](\text{NO}_3)_6 \cdot \text{H}_2\text{O}$ with ammonium carbonate solution at $\text{pH} \geq 8$, nitrate ions are substituted for carbonate ions with the formation of bismuth oxocarbonate $(\text{BiO})_2\text{CO}_3$ (ICDD PDF No. 84-1752) according to reaction:

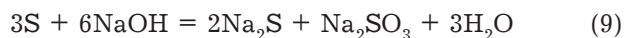


After annealing bismuth oxocarbonate at (380 ± 20) °C for 5 h, bismuth oxide was obtained. It was of chemically pure grade according to the results of chemical analysis (see Table 3). Bismuth(III) oxide obtained from bismuth oxocarbonate is composed of fused particles 0.5–0.7 μm in size (see Fig. 1, d). The specific surface area of bismuth(III) oxide is 4.40 m²/g, and its bulk density is 0.85 g/cm³.

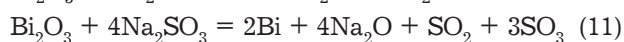
Obtaining high-purity metal bismuth

Hydrolytic processing of the metal bismuth of Bi 1 grade results in obtaining bismuth oxide of

specially pure grade. The method of practical interest is the formation of high-purity metal bismuth by bismuth oxide reduction in sodium hydroxide melt containing sulphur. After the addition of sulphur into solid hydroxide melt, sulphur disproportionation with the formation of sodium sulphide and sulphite proceeds:



After the addition of bismuth oxide into this solution, the following reactions take place [5]:



The studies give evidence that the reduction of bismuth oxide in sodium hydroxide melts in the presence of sulphur allows obtaining high-purity metal bismuth. The data presented in Table 4 show that the high characteristics of oxide reduction are achieved at the mass ratio of sodium hydroxide to bismuth in the oxide within the range of 0.8–1.6, sulphur to bismuth ratio within 0.2–0.5. With an increase in the ratio of

TABLE 4

Results of bismuth(III) oxide melting

Load and component ratio					Bismuth obtained, g	Bismuth recovery, %
Bismuth oxide	Sodium hydroxide, g	NaOH/Bi	Sulphur, g	S/Bi		
153	200	1.46	20	0.15	39.1	31.0
153	200	1.46	30	0.22	124.5	98.8
153	200	1.46	40	0.29	125.0	99.2
153	200	1.46	50	0.36	125.5	99.6
153	200	1.46	70	0.51	125.8	99.8
153 ^a	80	0.58	30	0.22	91.4	72.7
153	120	0.88	30	0.22	123.2	97.8
153	160	1.17	30	0.22	124.2	98.6
153	200	1.46	30	0.22	124.5	98.8
153	240	1.75	30	0.22	120.0	95.2
153	300	2.19	30	0.22	99.4	78.9
153	480	3.50	80	0.58	74.1	58.8
153	600	4.38	100	0.73	44.1	35.0
383	500	1.46	75	0.22	310.9	98.7

^a Very dense slag.

sodium hydroxide to bismuth above 1.5, bismuth concentration in the slag is observed to increase, which causes a decrease in recovery degree.

Bismuth(III) oxide of the specially pure grade in the amount of 893 g, obtained as a result of processing 1.0 kg of Bi 1 grade metal bismuth, was loaded at 400 °C during mixing into preliminarily molten and dehydrated sodium hydroxide (1.17 kg) containing 180 g of sulphur. Bismuth was reduced in the melt at 500 °C for 30 min (bismuth(III) oxide/sodium hydroxide /sulphur ratio is 1.00 : 1.31 : 0.20). Bismuth in the amount of 785 g is obtained. The results of its chemical analysis are shown in Table 5. According to GOST 10928-75, the obtained product corresponds to Bi 000 grade. The direct recovery of bismuth into product from bismuth oxide is 98.6 %.

CONCLUSION

It is shown that the dissolution of metal bismuth in nitric acid in the presence of ammonium nitrate at the molar ratio of ammonium to bismuth equal to 1.5–3.5, at a temperature of 70±5 °C, allows one to prevent the evolution of nitrogen oxides into the gas phase and to obtain the solution with high bismuth concentration.

It is determined that it is reasonable to conduct the hydrolytic treatment of bismuth-containing nitric acid solution in two stages for the purpose of purifying bismuth from impurity metals.

TABLE 5

Major component contents and impurities in metal bismuth

Parameter	Content, wt%	
	1	2
Bismuth	≥99.999	99.999
Lead	≤3 · 10 ⁻⁵	<5 · 10 ⁻⁶
Zinc	≤5 · 10 ⁻⁵	<1 · 10 ⁻⁵
Iron	≤3 · 10 ⁻⁵	<1 · 10 ⁻⁵
Antimony	≤1 · 10 ⁻⁵	<5 · 10 ⁻⁶
Copper	≤5 · 10 ⁻⁶	<1 · 10 ⁻⁵
Silver	≤5 · 10 ⁻⁶	<5 · 10 ⁻⁶
Arsenic	≤3 · 10 ⁻⁵	<1 · 10 ⁻⁵
Cadmium	≤1 · 10 ⁻⁶	<1 · 10 ⁻⁶

Note. Metal bismuth: 1 – according to GOST 10928-75, grade Bi 000; 2 – product of bismuth oxide reduction in sodium hydroxide melt in the presence of sulphur.

At the first stage, aqueous hydrolysis of the solution is carried out by adding it into water heated to 60 °C at the volume ratio water/bismuth-containing solution = 9 : 1, while at the second stage bismuth is additionally precipitated from the solution after aqueous hydrolysis by adding ammonium carbonate solution to pH 1 at 55±5 °C.

It is shown that hydrolytic processing of bismuth solutions in nitric acid solutions allows us to obtain bismuth oxohydroxonitrate [Bi₆O₅(OH)₃](NO₃)₅ · 3H₂O, bismuth nitrate pentahydrate Bi(NO₃)₃ · 5H₂O and bismuth(III) oxide of specially pure grade. As a result of bismuth(III)

oxide reduction in sodium hydroxide melt containing sulphur, high-purity metal bismuth is obtained.

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