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Preparation of High-Purity Nanometer Bismuth Trioxide from Silver-Zinc Slag

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Abstract: Silver-zinc slag, containing a lot of Bi, Ag, Cu, Zn, Pb and a little Au, has high comprehensive utilization value. This paper describes a preparation method of high-purity nanometer bismuth trioxide (Bi_2O_3) from silver-zinc slag by hydrometallurgical method. The results showed that Bi could be effectively leached out from silver-zinc slag using sodium chlorate, hydrochloric acid and sodium chloride as leaching agents, and the leaching rate of Bi was up to 99.03% under the optimum conditions. The contents of Pb^{2+} and Ag^{+} in $BiCl_3$ solution could be reduced to about 1mg/L by using silver-zinc slag as reductant and sodium iodide (NaI) as precipitant, respectively. Crystalline form of Bi_2O_3 is affected greatly by concentration of NaOH, conversion temperature and time. The suitable temperature of BiOCl converting to Bi_2O_3 was 90 ℃, and the suitable surfactant was polyvinyl alcohol. The average particle size of Bi_2O_3 obtained was about 86 nm, the purity of Bi_2O_3 was up to 99.75%, and the yield was 98.21%.

Introduction

Silver-zinc slag is a kind of scum formed from the process of collecting impurities such as Ag, Cu, Au, Pb and so on, using zinc as collector when refining bismuth (Bi) by pyrogenic process. Its main component is Bi, besides, it contains some Ag, Cu, Zn, Pb and a little Au, so it has high comprehensive utilization value. Usually there are three ways for silver-zinc slag treatment: pyrogenic process, pyro-hydro-metallurgical process and hydrometallurgical method [1]. The pyrogenic process is that Bi is removed firstly from silver-zinc slag by liquation, then the scoria is returned to silver converter or blast furnace. Its drawbacks are as follows: complex operation, ungovernable, low recovery rate for metals and serious enviroment pollution [2]. The pyro-hydro-metallurgical process are carried out as follows: a part of Bi is firstly removed from silver-zinc slag by liquation, then the residue is treated by oxidation leaching process to separate Bi further, thus precious metals can be concentrated in the residue for further extraction; Or the low-priced metal such as Bi is firstly separated from silver-zinc slag by chlorate oxidation leaching process, then the leaching slag is treated by reducing smelting to extract precious metals [3]. The procedure of hydrometallurgical method is that Bi and other low-priced metals are firstly leached and separated from silver-zinc slag by oxidation leaching process, and meanwhile, the precious metals such as Au and Ag are concentrated in the residue, then the extracts are treated further by hydrometallurgical method [4]. This method possesses the following distinguished advantages: simple process, less investment in equipment, high recovery rate for metal, obtaining not only metal products but also various kinds of chemicals [5].

Bismuth is a kind of “green metal” which can be used safely [6]. Bismuth trioxide (Bi_2O_3) shows many properties and becomes an important funcational material, which has been used extensively as electronic funcational material, flame retardant, catalyst, optical material, medical composite material, radiation protection material and so on [7,8,9], for example, as an additive in paints and cataphoresis, as a substitute for lead oxide in glass or porcelain [10]. More specifically, Bi_2O_3-based compounds are much better solid electrolytes than the well-known stabilized zirconia, because the face-centered cubic (fcc) δ-Bi_2O_3 exhibits the highest ion conductivity of all oxide ion conductors [11]. Typically, Bi_2O_3 is prepared via the oxidation of bismuth metal at 750℃~800℃ or via the thermal decomposition of carbonates or the addition of alkali-metal hydroxides to a bismuth salt solution [6,12,13]. Recently, various new preparation methods have been developed, such as electrodeposition [14], sol-gel process [8], plasma-chemical method [15], flame spray pyrolysis [16], laser vaporization-controlled condensation technique [17], polyol mediated synthesis [18], and hydro-thermal method [19], etc.

In this paper, we reported on the preparation method of high-purity nanometer Bi_2O_3 from silver-zinc slag by hydrometallurgical method. The optimum preparation conditions were investigated and the crystalline form and the particle size of Bi_2O_3 were examied.

Reaction principle and method

Composition of silver-zinc slag. The main components and chemical phase of silver-zinc slag are shown in Table 1 and Table 2, respectively.

Table1 The mass percentage of main components of silver-zinc slag [%]

Bi	Zn	Ag	Cu	Pb	Au	Sb
69.8~74.5	4.21~6.75	6.10~10.23	3.54	1.99	0.05~0.15	0.47

Table 2 The phase composition of Bi, Ag and Au in silver-zinc slag [%]

	Free form	Bi_2O_3	Bi_2S_3	Ag_2S	AgCl	Ag inclusion	Au inclusion	Other	Total content
Bi	47.69	22.45	0.011						70.151
Ag	10.37			0.127	0.078	0.015		0.15	10.74
Au	0.0819						0.0031	0	0.085

As shown in Table 1 and Table 2, the contents of Bi, Zn, Ag and Au are all higher, and Bi, Zn, Cu and Pb exist basically as metallic element, therefore, they are suitable to be leached by oxidation-acid method.

Leaching principle. The general oxidants are $FeCl_3$, $NaClO_3$ and HNO_3. The operating environment is bad and air is polluted seriously when HNO_3 is used as oxidant . While $FeCl_3$ is used as oxidant, there is a lot of iron ion remaining in the solution, which is unfavorable to the purification of Bi chemicals. Therefore, $NaClO_3$ is selected as oxidant. The reactions are as follows:

$$2\,Bi + ClO_3^- + (2n-1)\,Cl^- + 6\,H^+ \longrightarrow 2\,BiCl_n^{(n-3)-} + 3\,H_2O \quad n = 1\sim6 \qquad (1)$$

$$3\,Cu + ClO_3^- + (3n-1)\,Cl^- + 6\,H^+ \longrightarrow 3\,CuCl_n^{(n-2)-} + 3\,H_2O \quad n = 1\sim4 \qquad (2)$$

$$Zn + n\,Cl^- + 2\,H^+ \longrightarrow ZnCl_n^{(n-2)-} + H_2 \quad n = 1\sim4 \qquad (3)$$

$$Pb + n\,Cl^- + 2\,H^+ \longrightarrow PbCl_n^{(n-2)-} + H_2 \quad n = 2\sim4 \qquad (4)$$

At the same time, Au and Ag are oxidized partially. The reactions are as follows:

$$2\,Au + ClO_3^- + 7\,Cl^- + 6\,H^+ \longrightarrow 2\,AuCl_4^- + 3\,H_2O \qquad (5)$$

$$6\,Ag + ClO_3^- + 5\,Cl^- + 6\,H^+ \longrightarrow 6\,AgCl\downarrow + 3\,H_2O \qquad (6)$$

$$AgCl + Cl^- \longrightarrow AgCl_2^- \qquad (7)$$

Preparation of Bi_2O_3. In this paper, Bi_2O_3 was prepared by two-step method. The first step, $BiCl_3$ is hydrolyzed to prepare BiOCl by dilute alkali according to the following reaction:

$$BiCl_3 + 2\,OH^- \longrightarrow BiOCl\downarrow + H_2O + 2\,Cl^- \qquad (8)$$

The second step, BiOCl is transformed to Bi_2O_3 by concentrated alkali according to the following reactions:

$$BiOCl + NaOH \longrightarrow BiOOH\downarrow + NaCl \qquad (9)$$

$$2\,BiOOH \longrightarrow Bi_2O_3\downarrow + H_2O \qquad (10)$$

Because Bi^{3+} is hydrolyzed at pH range of 0.4～0.5, while other impurity metal ions are not hydrolyzed at the same pH range, the purification of Bi_2O_3 can be attained through controlling the end point pH value of hydrolysis. Moreover, the convertion of Bi_2O_3 can be realized at lower temperature, therefore, the calcinations process in traditional methods is omitted and high-energy consumption can be avoided.

Technological process. The technological process for Bi_2O_3 preparing from silver-zinc slag is shown in Fig. 1.

Experimental

Materials. Silver-zinc slag was obtained from Jiangxi Copper Company (Guixi, Jiangxi,China). Sodium chlorate ($NaClO_3$), hydrochloric acid (HCl) and sodium chloride (NaCl) were all industrial grade and used without further purification. Sodium iodide (NaI, analytical grade) and ammonia water (analytical grade) were purchased from Beijing Chemical Reagent Co. (Beijing, China). Polyethylene glycol (PEG-2000), sodium dodecyl benzene sulphonate and polyvinyl alcohol were of analytical grade and purchased from Guangfu Institute of Fine Chemicals (Tianjin, China). The water used in experiments was deionized water.

Experimental procedure. 100 g finely ground silver-zinc slag was added into a 250 mL three-necked flask, then a certain amount of $NaClO_3$, hydrochloric acid and NaCl were added too. After that, the mixture was reacted at a certain temperature for a certain time, then filtered and

$BiCl_3$ solution was obtained. The filtration residue (primary slag) was leached by adding another $NaClO_3$, hydrochloric acid and NaCl, and filtered again, the filtrate was returned for silver-zinc slag reaching and the filtration residue was further recovered due to it rich in Ag and Au.

A certain amount of silver-zinc slag was added to $BiCl_3$ solution, and reacted at a certain temperature and a certain pH value for a certain time, then a certain amount of NaI was added to the reaction mixture to react again. After that, the reaction mixture was filtered to obtain a refined $BiCl_3$ solution. After $BiCl_3$ solution was adjusted to a certain concentration, a suitable surfactant was added to the solution and a dilute ammonia water was slowly added to the mixture to react by controlling the end point pH value for a certain time, then pure BiOCl was obtained by filtering the reaction mixture and washing the filtration residue with dilute sulfuric acid. After a certain amount suitable surfactant was added into the three-necked flask with BiOCl, a concentrated NaOH solution was added to react for a certain time. The product Bi_2O_3 was separated by filtering and washed with deionized water, then dried at 100 ℃ to a constant weight.

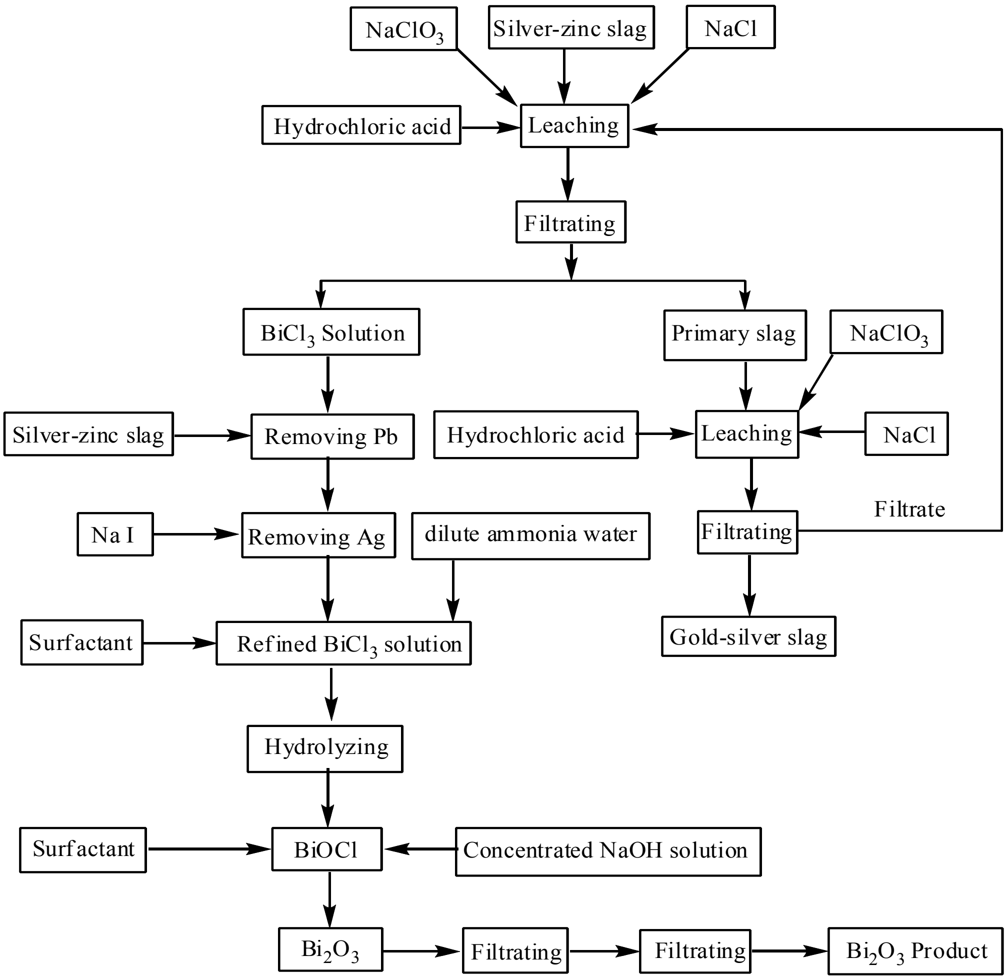


Fig. 1 Process flow diagram

Analytical method. The purity of Bi_2O_3 was determined by ICPS-7510 plasma emitting spectrometry and its yield was determined by chemical analysis. The microstructure of Bi_2O_3 was characterized by Rigaku D/ruax 2550 PC X-ray diffraction (Cu Ka, 40 kV, 250 mA). Measurements of particle size of Bi_2O_3 were performed based on laser diffraction combined with polarization intensity differential scattering. For this purpose, a Coulter LS230 equipped with a laser (750 nm, 5 mW) and a PIDS lamp (tungsten-halogen, 150 lumens at 2900 K) as well as 126 photodiode detectors were used.

Results and discussion

Influencing factors for Bi leaching. The Exploration experiments show that the main influencing factors for Bi leaching include mass of $NaClO_3$, volume of concentrated HCl, leaching temperature and time, mass of NaCl and ratio of solid to liquid. The leaching conditions were optimized by orthogonal design method and $L_{25}(5^6)$ table was chosen for the experiment. The optimum conditions are as follows: For 100 g silver-zinc slag, ratio of solid to liquid is 9~10：1, volume of concentrated HCl is 100~120 mL, mass of $NaClO_3$ is 12~15 g, mass of NaCl is 60 g, leaching temperature is 75~80 ℃, and leaching time is 4~5h.

The leaching rate of Bi increases with increasing mass of $NaClO_3$, and reaches above 98.5% when the mass of $NaClO_3$ is up to 12~15 g. At the same time, the low-priced metals such as Cu, Zn, Pb and so on, have also been dissolved out. When the mass of $NaClO_3$ still increases, Au and Ag may also been dissolved out. The addition of HCl not only prevents the hydrolysis of metal ions, but also increases the concentration of Cl^- to promote the leaching of Bi. But when the concentration of HCl is higher, $NaClO_3$ decomposes quickly and the consumption of raw materials increases. Moreover, the additon of NaCl can also increase the concentration of Cl^-which can promote nonferrous metal ions dissolving to form coordination ion, thereby promoting nonferrous metal leaching. But when the mass of NaCl is higher, it may also promote Ag and Au dissolving. In general, 10%～20% Au is leached out using $NaClO_3$ as oxidant. After being oxidized, Ag^+ reacts with $Cl^-$to form AgCl precipitate. When the concentration of $Cl^-$is higher, AgCl is dissolved to form $AgCl_{1+x}$ with Cl^-.

Under the optimum conditions, the leaching rate of Bi is up to 99.03%, the content of Ag and Au in residue are 73.15% and 1.12%, respectively. The composition of $BiCl_3$ solution is shown in Table 3.

Table 3 The composition of $BiCl_3$ solution [mg/L]

Element	Bi	Cu	Te	Zn	Pb	Fe
Concentration	96915.2	9243.2	3979.1	3401.5	1279.8	312.5

Element	Se	Ni	Ag	As	Sb	Sn	Ga
Concentration	123.5	70.4	45.7	33.8	29.4	17.5	3.99

Refining of $BiCl_3$ solution. The contents of Pb and Ag in $BiCl_3$ solution were all higher, Pb mainly exists in the form of H_2PbCl_4 and Ag in the form of $AgCl_{1+x}$ [20]. When $BiCl_3$ solution is hydrolyzed by adding dilute ammonia solution, Pb can be converted to be $PbCl_2$ and formed coprecipitation with BiOCl, and converted to be $Pb(OH)_2$ or PbO to enter the solid phase of Bi_2O_3 when using concentrated NaOH, leading to separation difficult. The relationship of Pb content between $BiCl_3$ solution and the product of Bi_2O_3 is shown in Table 4.

Table 4 Relationship of Pb content between $BiCl_3$ solution and Bi_2O_3

Pb content in $BiCl_3$ solution [mg/L]	0~2	2~10	10~30	30~100
Pb content of Bi_2O_3 [%]	0~0.002	0.002~0.01	0.01~0.03	0.03~0.05

As shown in Table 4, when Pb content in $BiCl_3$ solution is below 2 mg/L, the Pb content of Bi_2O_3 is below 0.002%.

It is found that when the content of Ag in Bi_2O_3 exceeds 0.02%, Bi_2O_3 is very easy to lose luster, even turns to be gray or grayish-brown. Although $AgCl_{1+x}$ may turn to be Ag_2O and Ag_2O is dissolved completely when pH＞13 during the procedure of conversation, it is difficult that Ag enter the solution completely, leading to most of them remaining in Bi_2O_3. The content of Ag is always in a range of 0.01%~0.05%.

Due to the acidity and Cl^- content of $BiCl_3$ solution higher, the common removing methods of Pb were difficult to meet the requirement, such as sulphate, phosphate, and oxalate, etc. The removal efficiency of Pb reduced by iron power or zinc power was also not ideal. It is found that precious metal ions can be reduced to be precious metal and enter to the residue when leaching liquor is reduced by silver-zinc slag, which can not only reduce the lose of Au and Ag, but also decrease the content of Pb in $BiCl_3$ solution [1]. Therefore, the removal of Pb through reduction reaction using silver-zinc slag as reductant was adopted in this paper. The results show that, when the ratio of solid to liquid of silver-zinc slag to $BiCl_3$ solution is 10 ∶ 1, the initial pH value is 0.3~0.4, agitation speed is 1000 r/min, and the leaching time is no more than 15 min, the content of Pb can be reduced to below 5 mg/L. Due to the lower solubility product of AgI ($Ksp=8.3\times10^{-17}$), NaI was adopted to remove Ag. The results indicate that, after removing Pb according to the above method, 1.2~1.4 times of the theory amount of NaI is added immediately to react for about 0.5 h, the contents of Pb^{2+} and Ag^+ can be reduced to about 1 mg/L.

Preparation of high-purity Bi_2O_3. Because the particle size of BiOCl has great influence to its conversion rate, it is necessary to control the particle size of BiOCl as small as possible. Fig. 2 shows effect of concentration of $BiCl_3$ solution on the particle size of BiOCl using a dilute ammonia solution as precipitator at room temperature. As shown in Fig. 2, the particle size of BiOCl decreases with increasing $BiCl_3$ concentration when concentration of $BiCl_3$ solution is below 0.3 mol/L, and increases with increasing $BiCl_3$ concentration when concentration of $BiCl_3$ solution is above 0.3 mol/L. The suitable concentration of $BiCl_3$ is 0.3 mol/L.

Fig. 3 shows effects of the end point pH value on the hydrolysis ratio of $BiCl_3$ and the purity of BiOCl.

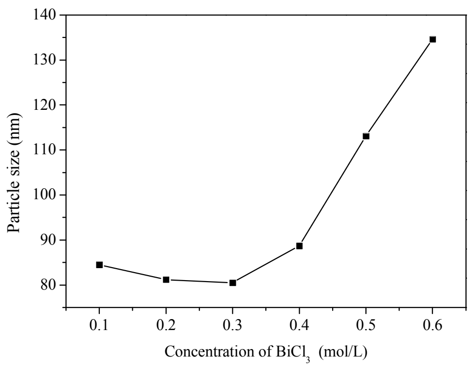


Fig.2 Effect of concentration of $BiCl_3$ on particle size of BiOCl

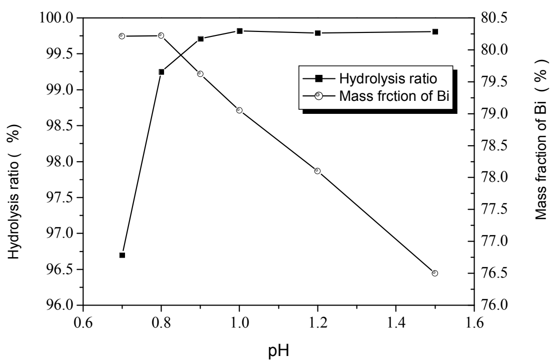
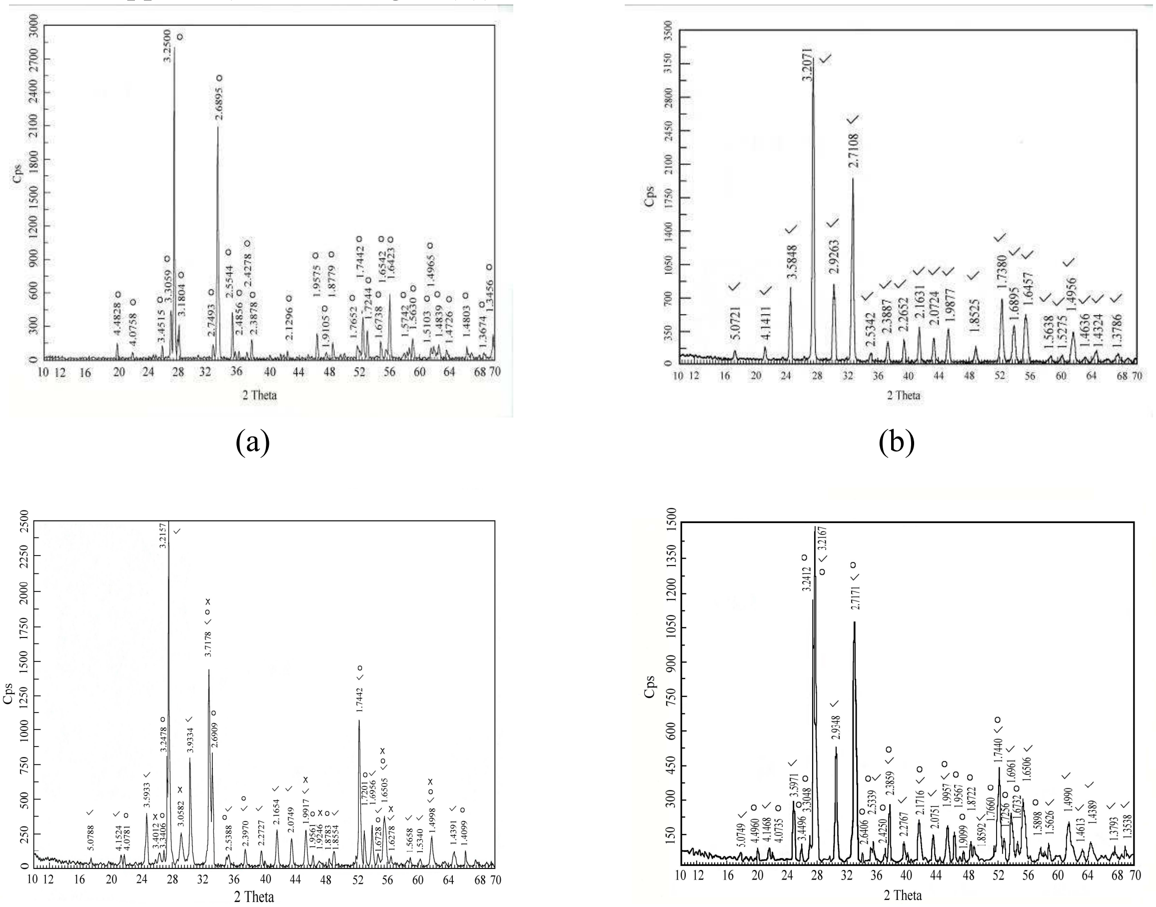


Fig. 3 Effects of pH value on hydrolysis ratio of Bi^{3+} and mass fraction of Bi in BiOCl

As shown in Fig.3, the hydrolysis ratio of $BiCl_3$ increases rapidly with increasing pH and reaches to 99.3% when pH=0.8, and to the maximum when pH=1.0. While the variation trend of purity of BiOCl is just the other way. When pH<0.8, the mass fraction of Bi in BiOCl is very close to the theoretical value of 80.244%, while when pH>0.8, it decreases obviously. This is because only Bi^{3+} can be hydrolyzed when pH<0.8, while pH>0.8, other metal ions can also be hydrolyzed to form coprecipitation with BiOCl [5,20]. Therefore, the end point pH value should be controlled to be 0.8. Moreover, it is found that dilute alkali should be adopted and should not be added too quickly, otherwise, the average particle size of BiOCl becomes large and particle size distribution is not homogenous. Hydrolyzed according to the above conditions, the particle size of BiOCl is controlled basically about 80 nm.

Fig.4 shows the XRD patterns of Bi_2O_3 obtained under different conditions. Bismuth trioxide has four polymorphs: monoclinic(or pseudo-orthorhombic) α-form, face centred cubic (fcc) δ-form, tetragonal β-form and body centred cubic (bcc) γ-form [12]. It can be seen that, when NaOH concentration is 4.0 mol/L, conversion temperature is 90 ℃ and reaction time is 2.5 h, the phase is pure α-Bi_2O_3; when NaOH concentration is 6.0 mol/L, conversion temperature is 105 ℃ and reaction time is 4.0 h, the phase is pure γ-Bi_2O_3; while when NaOH concentration is 3.0 mol/L, conversion temperature is 90 ℃ and reaction time is 2.0 h, the phase is a mixture of α-Bi_2O_3, γ-Bi_2O_3 and a little of $Bi_2O_{2.33}$, but when reaction time is prolonged to 2 h 40 min, the phase of $Bi_2O_{2.33}$ disappears (shown in Fig. 4 (d)).



(a) (b)

(c) (d)

Fig. 4 X-ray diffraction patterns of (a) α-Bi_2O_3(concentration of NaOH=4.0 mol/L, conversion temperature 90 ℃, time 2.5 h), (b) γ-Bi_2O_3(concentration of NaOH=6.0 mol/L, conversion temperature 105 ℃, time 4.0 h), (c) α-Bi_2O_3+γ-Bi_2O_3+ $Bi_2O_{2.33}$ (concentration of NaOH= 3.0 mol/L, conversion temperature 90℃, time 2.0 h), (d) α-Bi_2O_3+γ-Bi_2O_3 (concentration of NaOH= 3.0 mol/L, conversion temperature 90 ℃, time 2 h 40 min)

O— α-Bi_2O_3, ✓— γ-Bi_2O_3, ×— $Bi_2O_{2.33}$

Fig.5 shows effect of conversion temperature on the particle size of Bi_2O_3 when NaOH concentration is 4.0 mol/L, conversion temperature is 90 ℃, reaction time is 2.5 h and polyvinyl alcohol as surfactant. The results indicate that, the particle size of Bi_2O_3 increases with the increase of temperature, especially when the temperature is above 90 ℃, the increasing trend is more obvious. From the perspective of granularity controlling, conversion temperature should be lower, but the color of Bi_2O_3 is not flashy when temperature is below 90 ℃. Therefore, the temperature is determined to be 90 ℃.

Fig.6 shows effects of surfactants of polyethylene glycol-2000, sodium dodecyl benzene sulfonate, and polyvinyl alcohol on the particle size of Bi_2O_3. As shown in Fig.6, effect of polyvinyl alcohol is the best, its suitable dosage is 4×10^{-3} mol/L, and the particle size is about 86 nm. Due to high surface energy, small particles easily assemble each other to form large particles. Polyvinyl alcohol can be adsorbed on the surface of nanoparticles to decrease surface energy and increase steric hindrance between nanoparticles, thereby increasing the dispersity of particles.

Prepared according to the above conditions, the average particle size of Bi_2O_3 is about 86 nm, the purity of Bi_2O_3 is up to 99.75%, and the yield is 98.21%.

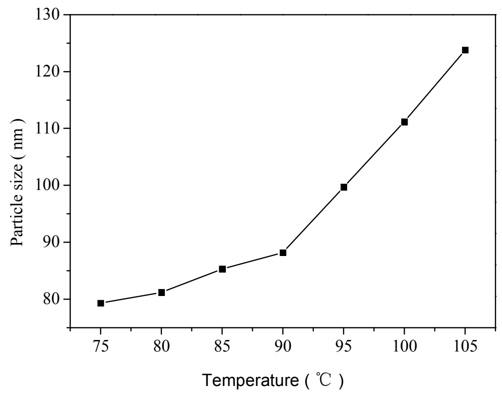


Fig. 5 Effect of conversion temperature on particle size

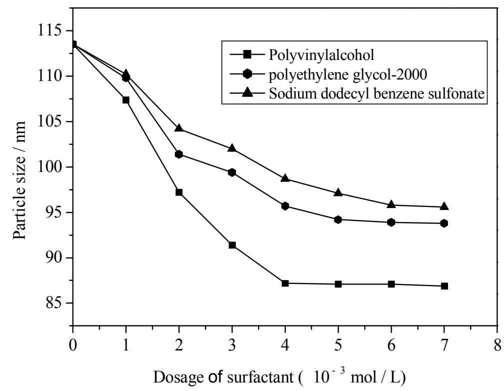


Fig.6 Effect of surfactant on particle size of Bi_2O_3

Conclusions

Bismuth can be leached effectively from silver-zinc slag by hydrometallurgical method. The optimum conditions are as follows: For 100 g silver-zinc slag, ratio of solid to liquid is 9~10：1, volume of concentrated HCl is 100~120 mL, mass of $NaClO_3$ is 12~15 g, mass of NaCl is 60 g, leaching temperature is 75~80 ℃, and leaching time is 4~5 h, the leaching rate of Bi is up to 99.03%, the content of Ag and Au in residue are 73.15% and 1.12%, respectively.

Pb in $BiCl_3$ solution can be effectively removed by reduced using silver-zinc slag as reductant, and Ag can be removed by adding NaI to form AgI, the contents of Pb^{2+} and Ag^+ can be reduced to about 1 mg/L. When $BiCl_3$ solution is hydrolyzed to form BiOCl with dilue ammonia water, the suitable concentration of $BiCl_3$ solution is 0.3 mol/L, and the end point pH value should be controlled to be 0.8, the particle size of BiOCl can be controlled basically about 80 nm.

In the conversion process of BiOCl to Bi_2O_3 with concentrated NaOH, crystalline form of Bi_2O_3 is affected greatly by concentration of NaOH, conversion temperature and time. The suitable conversion temperature is 90 ℃, and the suitable surfactant is polyvinyl alcohol. The average particle size of Bi_2O_3 is about 86 nm, the purity of Bi_2O_3 is up to 99.75%, and the yield is 98.21%.

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