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Preparation of clarificant for glass from As-Sb dust①

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Abstract: The arsenic and antimony dust arisen from the volatilization of anode slime in the electrolysis of copper and lead was used as raw materials. The process of direct volatilization or reduction-oxidation volatilization was employed to produce the mixture of As_2O_3 and Sb_2O_3, and then Na_2SO_4 was added to produce clarificant for glass. The optimizing technology conditions which were obtained from the test of preparing the mixture of pure As_2O_3 and Sb_2O_3 by the volatilization method are reaction temperature 900 ℃ and reaction time about 30 min. The glass clarificant produced meets industrial application standard.

Key words: clarificant for glass; arsenic and antimony dust; anode slime **Document code:** A

1 INTRODUCTION

In nonferrous metallurgy, during the process of roasting and smelting, arsenic and antimony usually enter dust[1]. If no measures are taken to recover arsenic and antimony, the dust will not only cause environment pollution, but also leads to wasting in resources.

The recovery of arsenic and antimony from As-Sb dust can be realized by transforming arsenic and antimony dust into As_2O_3 and Sb_2O_3 or arsenate and antimonate, such as $Cu_3(AsO_4)_2$, Na_3AsO_4 and $NaSb(OH)_6$ etc. There are two methods, low temperature chlorinating-distillation[2] and reduction-chlorinating-leaching[3], to deal with As-Sb dust. The former can separate arsenic and antimony thoroughly and produce As_2O_3 and Sb_2O_3. Copper arsenate can be directly produced by the latter. In order to delimit arsenic pollution and utilize arsenic and antimony in dust, the method utilizing As-Sb dust directly as clarificant for glass has been tested[4~6]. In this paper direct volatilization and reduction-oxidation volatilization were employed to produce mixture of As_2O_3 and Sb_2O_3, then Na_2SO_4 was added to produce clarificant for glass.

The material used in the experiment was As-Sb dust obtained by volatilizing the copper anode slime and the chemical composition of dust is listed in Table 1.

In the dust, arsenic and antimony exist mainly in the form of As_2O_3 and Sb_2O_3, and a little in the form of As_2O_5 and Sb_2O_5.

The chemical composition of STL type clarificant for glass used in glass industry is listed in Table 2.

According to Table 2, the dust can be used as clarificant for glass if the content of Fe and Cu is reduced so that the content of FeO is less than 0.05%.

Table 1 Chemical composition of As-Sb dust(%)

Element	As	Sb	Fe	Cu	Bi
Content	43.83	24.81	0.83	0.28	0.10
Element	**Cr**	**Pb**	**Mn**	**Sn**	
Content	0.007	5.18	0.001	0.005	

Table 2 Chemical composition of clarificant for glass (%)

Type	$As_2O_3 + Sb_2O_3$	Na_2O	SO_3	
STL-1	≥42	≥16	≤18	
STL-2	≥40	≥18	≤12	
F	25.5 ± 2	13.5 ± 2	30 ± 2	
Type	**FeO**	**Cu**	**Cr**	**H_2O**
STL-1	≤0.05		≤0.002	≤4
STL-2	≤0.05		≤0.002	≤4
F	≤0.06	≤0.005		

2 EXPERIMENTAL PRINCIPLE AND METHOD FOR PREPARATION

2.1 Direct volatilization method

In thermodynamics, the relationship between vapor pressure and temperature can be described as the following equations[7].

For Sb_2O_3:

$\lg p = 14.320 - 10\,357/T$ (cubic system, 450 ~ 550 ℃) (1)

$\lg p = 13.443 - 925/T$ (rhombic system,

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550 ~ 650 ℃) (2)

$$\lg p = 7.443 - 3\,900/T \quad \text{(liquid)} \quad (3)$$

For As_2O_3:

$$\lg p = 13.03 - 5\,282/T \quad (4)$$

According to the equations, vapor pressure of Sb_2O_3 and As_2O_3 at different temperature can be calculated, which is listed in Table 3. Table 4 lists melting points and boiling points of As, Sb, Fe and Cu.

Table 3 Vapor pressure of Sb_2O_3 and As_2O_3 at different temperature

Temperature/ ℃	200	300	350
Vapor pressure of Sb_2O_3/ Pa		0.08	273.3
Vapor pressure of As_2O_3/ Pa	72.9	6 457	35 646
Temperature/ ℃	385	400	600
Vapor pressure of Sb_2O_3/ Pa	6 431.8	23 953.8	101 324.7
Vapor pressure of As_2O_3/ Pa	100 600	151 901	

Table 4 Melting points and boiling points of As, Sb, Fe and Cu

	As	Sb	Fe	Cu
Melting point/ ℃		631	1 536	1 083
Boiling point/ ℃	603	1 635	3 070	2 570

As shown in Table 3 and Table 4, the vapor pressure of As_2O_3 and Sb_2O_3 in the As-Sb dust is high, and boiling point of As and Sb is far lower than that of Fe and Cu. Therefore, by means of volatilizing the dust, As and Sb transform into gas phase, while Fe and Cu remain in the residue. Thus, As_2O_3 and Sb_2O_3 are separated from the impurities such as Fe and Cu by the direct volatilization method.

The flowsheet to separate impurities of Cu and Fe, etc, for the preparation of clarificant is shown in Fig.1.

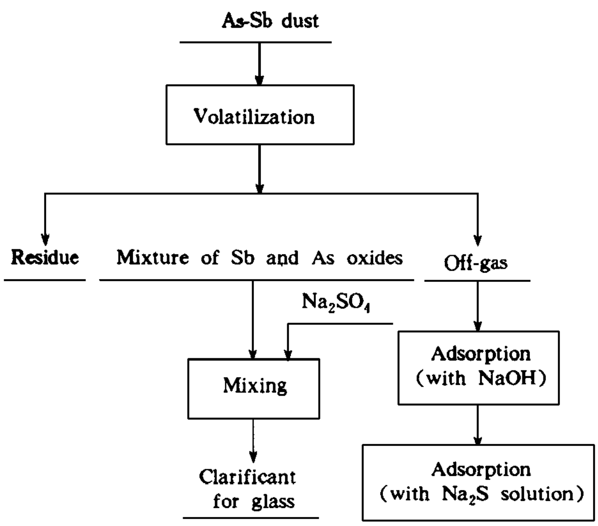

Fig.1 Flowsheet for preparation of glass clarificant

2.2 Reduction-oxidation volatilization method

In terms of the characteristic that the reduction and oxidation temperatures of As and Sb are lower than those of Cu and Fe, As_2O_3 and Sb_2O_3 in dust are firstly reduced as element As and Sb, i.e.

$$2Sb_2O_3 + 3C = 4Sb + 3CO_2 \quad (5)$$

$$2As_2O_3 + 3C = 4As + 3CO_2 \quad (6)$$

then, controlling temperature, As and Sb are oxidized as arsenic and antimony oxides by air.

$$4As + 3O_2 = 2As_2O_3 \quad (7)$$

$$4Sb + 3O_2 = 2Sb_2O_3 \quad (8)$$

The flowsheet for the reduction-oxidation volatilization method is basically identical to that for the direct volatilization method, except for adding reducing agent carbon in the As-Sb bearing dust.

3 RESULTS AND DISCUSSION

The relationships between reaction temperature and reaction time of the volatilization for arsenic and antimony by direct volatilization method are given in Fig.2 and Fig.3 respectively. The relationship between reaction temperature and chemical composition of volatile substance is listed in Table 5.

Fig.2 and Fig.3 show that the volatilization of As and Sb is over 80 %, if temperature reaches 900 ℃ and reaction lasts 30 min. It can be seen that the impurity Fe and Cu in volatile substance can be lowered

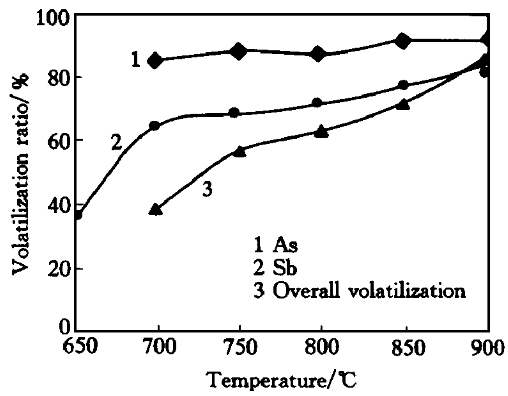

Fig.2 Relationships between volatilization and reaction temperature

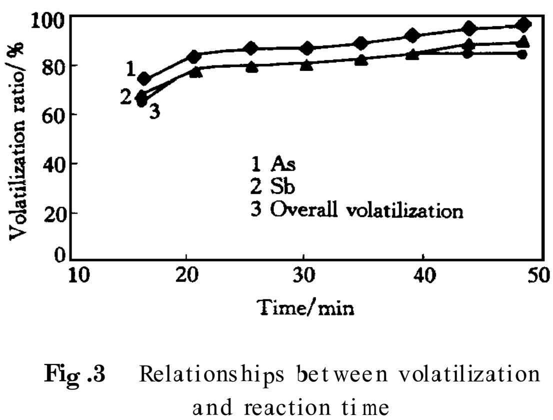

Fig.3 Relationships between volatilization and reaction time

Table 5 Relationships between chemical composition of volatile substance and reaction temperature

Temperature / ℃	Composition/ %				Overall volatilization / %
	As	Sb	Fe	Cu	
700	58.36	15.19	0.067	0.038	64
750	56.64	20.66	0.055	0.026	68
800	53.07	21.83	0.043	0.026	72
850	52.52	23.18	0.022	0.015	78
900	48.06	25.59	0.022	0.016	84

to 0.022 % and 0.016 %, respectively.

The optimized conditions for direct volatilization can be described as following: the reaction temperature is controlled at 900 ℃, reaction time is about 30 min. Na_2SO_4 is added in proportion as listed in Table 2 into As_2O_3 and Sb_2O_3 mixture collected in the above reaction, thus the clarificant for glass is prepared. The chemical composition of the clarificant is listed in Table 6.

Table 6 Chemical composition of clarificant for glass obtained by direct volatilization

Type	As	Sb	Na_2O	FeO	Cu
Test-1	30.45	16.23	16	0.0179	0.01
Test-2	28.39	15.11	18	0.0167	0.009

In the process of reduction-oxidation volatilization[8], at first, 2 % ~ 6 % of reductant, carbon powder, is added into As-Sb dust, Sb_2O_3 and As_2O_3 are reduced into element As and Sb, and then As and Sb are turned into As_2O_3 and Sb_2O_3 again. Later, the mixture of As_2O_3 and Sb_2O_3 obtained is mixed with Na_2SO_4 in proportion as listed in Table 2. Thus qualified clarificant for glass is prepared.

4 CONCLUSION

In this experiment, As-Sb dust is used as raw material to prepare clarificant for glass by means of volatilizing. Pure As_2O_3 and Sb_2O_3 are prepared by volatilization method, then Na_2SO_4 is added in proportion into their mixture, thus the clarificant for glass is obtained. The optimized technological conditions are reaction temperature at 900 ℃ and reaction time about 30 min. The process is simple, and the cost of raw material is very low. It will not only prevent the environment from being polluted by poisonous arsenic, but also recycle useful resources.

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