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Investigation Of The Process Of Reagent Refining Of Crude Antimony From Lead.

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ABSTRACT

In this article, the behavior of lead in the known methods of reagent refining of antimony has been studied in order to optimize the process in the direction of reducing lead content in the metal. Refining of crude antimony is carried out in several variants. Industrial methods of refining sodium sulfate, sodium carbonate, alkali and their mixtures have been tested. The results of experiments and X-ray phase analysis of materials are presented.

Keywords: crude antimony, refining, metal antimony.

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INTRODUCTION

At present, in the world market antimony is one of the demanded small metals. Its world demand is more than 80 thousand tons per year [1]. The main types of commodity products of high demand are antimony metal and its trioxide. Antimony trioxide is obtained from higher grades of metal. Therefore, the production of metallic antimony with small amounts of impurities is an actual task. One of the hard-to-remove impurities from antimony is lead. Previously, technical grades of metallic antimony allowed up to 5% of lead [2]. To obtain higher grades of metal, it was required to remove the lead to a residual content of 0.1% in the metal by electrolytic refining. Other impurities such as arsenic, iron and tin were removed by reagent (fire) refining. From the point of view of saving material and energy costs, the methods of fire metal refining are considered effective. Electrolytic refining of antimony is characterized by the formation of large quantities of effluent requiring utilization, the duration of the process and the consumption of electricity. This method of refining antimony is justified when obtaining anode slimes enriched in gold. In this regard, the study of methods of reagent refining of antimony to remove lead to the required content is relevant in the field of metallurgy of lead.

Our research is aimed at studying the behavior of lead in the known methods of reagent refining of antimony in order to optimize the process in the direction of reducing the lead content in the metal.

Refining of crudeantimony is carried out in several variants. Industrial methods for refining sodium sulfate, sodium carbonate, alkali and mixtures thereof have been tested (Table 1). The initial antimony contained the main impurities,%: Pb 2.23-3.03; Sn 0.58-1.29; As 0.11; Fe 0.86.

Table 1 - Conditions and results of refining of crude antimony with sodium sulphate, soda and alkali

Experiment No.		Mass of fluxes, %			Melting conditions, τ_{min}/t,°C	Alloy yield, %	Content in alloy, %				
		Na_2SO_4	Na_2CO_3	NaOH			Sb	Pb	Sn	As	Fe
1	1	-	-	10	15/880						
	2	-	-	10	20/880						
	3	-	-	10	10/890	55.97	96.54	2.23	0.43	<0.001	0.034
2	1	19	-	-	30/950						
	2	-	19	19	25/850	66.28	93.60	2.92	0.40	<0.001	0.049
3	1	19	-	-	30/900						
	2	-	19	-	25/900	62.28	97.14	3.03	0.30	<0.001	0.036
4	1	-	-	10	20/670	86.0				<0.001	0.48
5	1	20	-	-	40/958	90.55	96.60	2.09	0.58	0.06	0.075
6	1	-	10	-	20/911	80.67				<0.001	0.032
7	1	-	8	8	20/702	89.59	92.61			<0.001	0.70
8	1	-	10	10	20/696	96.10	96.47			<0.001	0.68
9	1	-	20	20	20/923	86.00				<0.001	0.66
Note: Experiments Nos. 1, 2 and 3 were carried out in stages 3 and 2; The remaining experiments are in stage 1.											

The use of soda and soda with alkali allowed the removal of arsenic to its content <0.001%. However, the lead content is retained as in the original metal.

With the use of sodium sulfate, as in traditional methods of refining, antimony has been purified from iron to a content of 0.075%.

In order to reduce the melt temperature during refining as a flux, we tested an equimolar mixture of sodium and potassium chlorides having a melting point of less than 500 °C (Table 2). The initial antimony contained the following amount of basic impurities,%: Pb 3.03; Sn 1.29; As 0.108; Fe 0.86.

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Table 2 - Conditions and results of antimony refining with a mixture of KCl, NaCl, Na_2CO_3

Experiment No.	Mass of fluxes, %			Melting conditions, τ_{min}/t,°C	Alloy yield, %	Content in alloy, %				
	KCl	NaCl	Na_2CO_3			Sb	Pb	Sn	As	Fe
1	10	10	–	30/680	83.60	96.58	3.19	0.044	0.066	0.020
2	10	10	–	30/667	83.00	96.60	3.08	0.062	0.090	0.016
3	10	10	10	20/678	76.67	96.76	3.03	0.085	<0.001	0.016
4	12	12	6	20/650	87.20	96.80	3.06	0.051	0.009	0.017

The use of a mixture of salts of sodium and potassium chlorides gave a significant effect in the process of purifying antimony from impurities:

A) Temperature of the melt decreased to 650 - 680 °C, this reduced the evaporation of antimony and increased the yield of the alloy to 96.8%;
B) Refining of Sb from tin to its content of 0.044-0.085% and iron to 0.016-0.020%; The purification of antimony from arsenic is also at a very high level.

Calcium chloride was used to refine antimony from tin. The choice of reagent is based on the high volatility of $PbCl_2$ (t_K = 953 °C) and good slagability of Ca in the form of CaO. In order to form CaO, antimony trioxide was introduced into the charge in an excess to carry out the reaction:

$$3Pb+3CaCl_2+Sb_2O_3 \rightarrow 3\,PbCl_2\uparrow+3CaO+2Sb \quad (1)$$

The antimony alloy to be refined contained,%: Sb 92.61, Pb 2.58, Sn 0.58; As 0.026; Fe 0.09.

In the process of refining of crude antimony by calcium chloride, the concentration of lead, tin and other impurities decreases (Table 3 and 4), however, it is not sufficient to obtain brandy antimony in lead. In addition, the lead chloride recovered during the refining process will require a good purification of the gas phase in the dust collection system.

Table 3 - Antimony refining with calcium chloride

Experiment No.	Mass of fluxes, %		Melting conditions, τ_{min}/t,°C	Alloy yield, %	Content in alloy, %				
	$CaCl_2$	Sb_2O_3			Sb	Pb	Sn	As	Fe
1	15	15	20/856	76.12	98.59	1.26	0.070	0.026	0.016
2	25	25	20/757	67.57	97.85	0.82	0.050	0.026	0.013
3	30	15	40/760	69.06	98.39	1.32	0.067	0.012	0.015
4	34	15	20/752	77.61	97.68	0.88	0.053	0.012	0.012
Note: The refined alloy concentration of calcium is 0.006%.									

The maximum degree of antimony purification from lead was 78.5% (experiment No. 2). But the losses of antimony with refining slags are significant -15-18%.

Table 4 - Extraction of antimony and impurities in refined metal

Experiment No.	Extraction degree, %				
	Sb	Pb	Sn	As	Fe
1	81.04	37.17	9.19	76.12	13.53
2	71.39	21.48	5.83	67.57	9.76
3	73.37	35.33	7.98	31.87	11.51
4	81.86	26.47	7.09	35.82	10.35

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Thus, the refining of crude antimony from lead by calcium chloride does not make it possible to obtain a metal of the required purity.

According to thermodynamic calculations, mentioned by S.M. Melnikov [2, p.69], it is possible to remove lead and tin by elemental sulfur in the form of sulphides. However, in the industry, antimony sulfide (croudum) or sulfide antimony concentrate is used. In this case, the lead from antimony is removed to a content of 0.8-1.3%. Experimental work on the refining of antimony by elemental sulfur.

Table 5 - Refining of crude antimony by elemental sulfur

Experiment No.		Mass of sulfur,%	Melting		Alloy yield, %	Matte yield, %	Content in alloy, %				
			τ_{min}	t,°C			Sb	Pb	Sn	As	Fe
1	*						93.54	3.64	0.151	0.016	0.014
		15	20	678	87.5	15.00	95.47	0.55	0.050	<0.001	0.013
2	*						93.54	3.64	0.151	0.016	0.014
		20	20	680	57.7	45.60	96.40	0.24	0.041	<0.001	0.015
3	*						96.75	2.21	0.45	0.23	0.057
		25	25	680	67.33	26.33	97.66	0.29	0.11	0.038	0.056
4	*						94.23	4.19	0.084	<0.001	0.045
		30	40	680	70.00	23.67	98.33	0.603	0.021	<0.001	0.046
5	*						94.20	3.86	0.043	<0.001	0.043
		30	40	680	66.00	10.00	98.80	0.59	0.023	<0.001	0.040
Note: * Original alloys											

The results on the refining of crude antimony from lead by elemental sulfur (Table 5) significantly exceed those given in Table 3. The obtained antimony in the impurity content corresponds to the grade of Cy2. The optimum for sulfur consumption is in the range of 20-25% of the mass of crude antimony. The low yield of the refined alloy is explained by the formation of matte (antimony sulphide), which can be used in subsequent smelting, which will avoid losses of antimony with matte [3].

The refining of antimony from lead by a reagent method has been widely studied by scientists of the PRC. To remove lead, oxides of phosphorus, boron and silicon are proposed in a mixture with sodium salts (Na_2CO_3, NaCl).

The process claimed for the refining from lead includes treatment of antimony with a mixture of hydroxyl acids of phosphorus and sulfuric acid with a nitrogen purge at the melting point of antimony. During the melting of hydroxyl acids of phosphorus (meta-, ortho-, pyrophosphoric acid) in a mixture with sodium salts, the polymerization of phosphates proceeds [4] andas a result, antimony is refined to a residual lead content of 0.1-0.2%.

Phosphorus pentoxide was also used in a mixture with sodium carbonate [5]. Antimony refining at 8000 ºC was achieved to lead content of 0.015% against its initial content in the crude metal - 4%. It is necessary to maintain the ratio P_2O_5: Na_2CO_3 = 3: 1. The rate of the refining mixture is 20% of the weight of the metal.

The processes of refining crude antimony from lead with ammonium dihydrogen phosphate have been studied. The thermal behavior of the mixture is measured by thermo gravimetric TG/DTA assays. The combustion products of the $NH_4H_2PO_4$ and PbO mixture of the following molar ratio of 2.5:3, obtained at 750 ºC for 30 minutes, are $Pb_2P_2O_7$ and $Pb_5P_4O_{15}$. Moreover, with the molar ratio $NH_4H_2PO_4$:Sb_2O_3 = 2.5:1 at 750 °C for 30 minutes, $SbPO_4$ was obtained. At 850 °C, as a result of the interaction of $SbPO_4$ and PbO, $Pb_{14.67}Sb_{1.33}(PO_4)_{12}$ is formed. This in turn proves that the complex compound $Pb_{14.67}Sb_{1.33}(PO_4)_{12}$ is more stable at higher temperatures than $SbPO_4$. I.e. when refining with phosphate compounds, stable phosphate compounds of lead are formed, easily separated from the metallic phase [6]. To separate the lead, authors of the above-mentioned research carried out a variety of studies. The interactions of BPO_4 and PbO and Sb_2O_3

have also been studied. As a result of sintering of a mixture of BPO_4 and PbO at 850 °C for 30 minutes, amorphous products were obtained, the product of $Pb_5(PO_4)3Cl$ crystal structure was obtained by sintering the mixture in the presence of sodium chloride. In the interaction of BPO_4 with Cb_2O_3 at 850 ºC, compounds of the crystal structure of $SbPO_4$ and $SbOPO_4$ were obtained. However, amorphous products were obtained in the presence of sodium. Thus, it can be asserted that the composition and crystal structure of the products obtained depend on the BPO_4 flow [7]. Metasodium phosphate was used to remove lead from antimony. The refining process was carried out at 700-1000 °C to obtain an antimony and lead phosphate melt [8].

All methods of refining antimony, as argued by the authors of the article, with compounds of phosphorus are more aimed at the formation of stable lead phosphates than antimony. In connection with this, we also carried out research on the refining of antimony with phosphorus compounds. But not only to determine the degree of refining of antimony from lead, but also to study the yield of commodity metal.

From the point of view of the convenience in the application of industry, experiments on the refining of antimony from lead were carried out with sodium hexametaphosphate. The phosphate content of sodium hexametaphosphate in P_2O_5 recalculation is more than 63% (i.e., P_2O_5/Na_2O ratio = 1.7-2.0). Also, hexametaphosphate sodium is a widely used product of phosphorous production. Experiments on the use of sodium hexametaphosphate as a refining agent for crude antimony from impurities showed the possibility of deep purification of the metal not only from lead, but also from tin and iron (Table 6).

Table 6 - Results of refining with sodium hexametaphosphate

Experiment No.	Flow $(NaPO_3)_6$, g	Metal yield,%	Content of elements in refined metal,%				
			Sb	Pb	Sn	Fe	As
1	20	94.3	98.42	0.800	0.60	0.18	<0.001
2	25	92.0	98.80	0.600	0.50	0.10	<0.001
3	30	90.1	99.01	0.420	0.56	0.008	<0.001
4	35	88.5	99.92	0.020	0.08	0.005	<0.001
5	40	87.3	99.95	0.013	0.03	0.005	<0.001
6	50	86.5	99.96	0.012	0.02	0.005	<0.001

At the expense of hexametaphosphate 40-50 g per 100 g of nickel metal antimony of the grade Sy00 was obtained. The yield of the metal is 86-88%. Also, to obtain the highest grades of antimony, a high consumption of reagent is required. The remaining amount of antimony passes into the slag.

X-ray phase analysis of slag (Figure 1) showed the presence of lead and antimony in the form of phosphates, also part of the antimony is in the form of oxides (Table 7), i.e. the loss of antimony with slag is due to the formation of phosphates and the dissolution of antimony oxides in the slag melt. Tin in the slag is present in the form of oxides.

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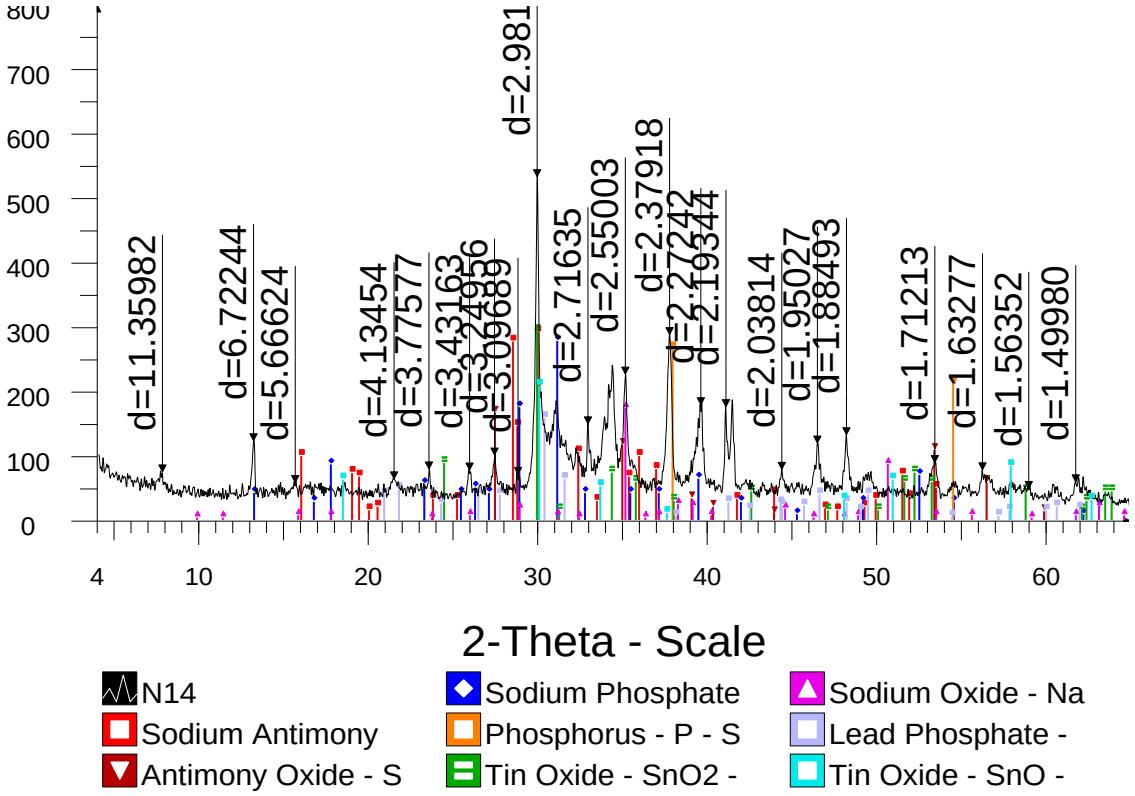

Figure 1- Diffraction pattern of slag refining hexametaphosphate

Table 7 - Results of semi-quantitative X-ray phase analysis of crystalline phases

No.	Phase description	Equation	Content, %
1	Sodium Antimony Oxide Phosphate	$NaSbOxPO_4$	28.9
2	Antimony Oxide	Sb_2O_4	16.5
3	Sodium Phosphate Oxide	$NaPO_3$	13.8
4	Phosphorus	P	13.2
5	Tin Oxide	SnO_2	5.8
6	Sodium Oxide	Na_2O_2	8.6
7	Lead Phosphate	$Pb_9(PO_4)_6$	7.9
8	TinOxide	SnO	5.2

Thus, the results of studies of reagent refining of antimony showed that removal of lead to the required content is impossible with the refining of antimony with metal chlorides and sulfur. When refining antimony with phosphorus compounds, it is possible to obtain a metal with a content of 0.012% against its initial content in the metal of 1.5%.

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