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Lead and tin removal from antimony metal by refining process with phosphorus compounds

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Abstract

The fire refining processes for antimony with the objective to primarily remove tin and lead as much as to receive respective residuals of 0.002% and 0.02% in the metal are multistage processes, associated with significant antimony losses during the slag phase, particularly when deep treatment for tin removal. This effect is observed due to the very close thermodynamic affinity of tin and antimony for oxygen. The present article concerns achieving the deep lead and tin removal from the antimony-bearing substance along with the decrease in antimony losses by slag and gases and studies refining with the mixture of sodium dihydrogen phosphate and phosphorus acid for antimony recovery. The reacting agent for the crude antimony refining to remove lead and tin was made from the preparatory mixture of sodium dihydrogen phosphate and phosphorus acid, taken in the certain ratio, and dehydrated. Following the addition of the prepared flux into the rough antimony, mixture was placed into the alundum crucible and heated in the muffled furnace with the observance of the certain temperature and time regime. The reported research has resulted in the optimal composition for refining antimony to remove lead and tin. Under optimal refining conditions, has been received the refined antimony metal with the remaining lead and tin as low as 0.015-0.008% and 0.005-0.001% respectively.

Key words: PRIMARY ANTIMONY METAL, REFINING, LEAD, OIL

Introduction

At present, the bulk of antimony produced is mainly consumed for antimony trioxide required for the further production of flame retardants. For high products of antimony trioxide, the only suitable metal is that of Sb99.65 grade or Sb99.85 grade as the impurities in it do not exceed 0.35-0.15%. Table 1 shows the chemical compositions of antimony grades by one of the world's leading producers.

The production of these metal grades requires the multistage refining for removing such impurities as arsenic, iron, tin, lead, bismuth and selenium. This causes the increase in the antimony metal prime cost. However, the involvement of high-quality antimony concentrates with a low content of impurities in the metallurgical process makes it possible to decrease the cost of metal, which is being practiced in the antimony production of China (Table 2).

Moreover, metallic antimony low cost production is not achievable if antimony concentrate is the byproduct of lead processing – the slag from lead refining, which

contains lead and tin in the range of 0.2-0.8%. This is explained by the fact that antimony concentrate with 45-47.55 % Sb and the chemical composition of impurities as much as 0.2-0.73 % Sn, 0.25-0.77 % Pb, 0.12-0.3 % As, 0.34 % Fe is smelted into the rough metal, which is 90-96% pure but containing not less than 0.4-1.4 % Sn, 0.5-1.5 % Pb, 0.1-0.3 % As and 0.4-0.6 % Fe. In addition to arsenic, which partially passes into the slag phase, all other impurities are reduced and concentrated in the rough metal. For the purpose of the antimony material further treatment for tin and lead decrease to a residual contents of 0.002 % and 0.02 % respectively, it is necessary to carry out the multi-stage fire refining directed primarily to tin removal and followed by electrolytic refining to remove lead. Due to the close thermodynamic affinity of tin and antimony for oxygen (Table 3), antimony losses occur in the slag phase during the tin-removing fire refining, they are especially large when with deep removal of tin.

The electrolytic method for antimony refining to remove lead is economically justified on condition that

Table 1. Metal antimony quality indicators (Hsikwangshan Twinkling StarCo., Ltd)[1]

Grade	Chemical composition, %								
	Sb \geq	Content of impurities \leq							
		As	Fe	S	Cu	Se	Pb	Bi	Total impurities
Sb99.90	99.9	0.02	0.015	0.008	0.01	0.003	0.03	0.003	0.1
Sb99.85	99.85	0.05	0.02	0.04	0.015	—	—	0.005	0.15
Sb99.65	99.65	0.1	0.03	0.06	0.05	—	—	—	0.35
Sb99.50	99.5	0.15	0.05	0.08	0.08	—	—	—	0.5

Table 2. Composition of antimony concentrate of PRC Huachang Group Company [2]

Grade	Sb, % \geq	Content of impurities, % \leq						
		As/Sb	Pb/Sb	Cu	Se	Sn	Cd	Bi
First	60	0.8	0.25	0.01	0.005	0.003	0.005	0.003
Second	50	0.8	0.30	0.01	0.005	0.003	0.005	0.003
Third	35	0.9	0.35	0.005	0.003	0.002	0.005	0.003

Table 3. Comparison of thermodynamic affinity of antimony, lead and tin for oxygen

Element and compound	ΔZ^0 , ccal/mol			
	800 °C	900 °C	1000 °C	1100 °C
Pb → PbO	-55.0	-50.7	-46.6	-42.9
Sb → Sb ₂ O ₃	-66.9	-63.3	-59.6	-56.4
Sn → SnO	-84.4	-79.4	-74.3	-69.3

the processed antimony material contains noble metals and is followed by the production of anodic sludge regarded as a concentrate of precious metals.

Considering the all above-said, it follows that the urgent problem in the sphere of antimony metallurgy is the development of the methods for simultaneous removal of tin and lead from antimony material with refining of minimal costs. In connection with this, we would like to note the contribution of the Chinese publications to the development of the antimony fire refining processes for lead removal. They offer oxides of phosphorus, boron and silicon to be applied in a mixture with sodium salts (Na₂CO₃, NaCl).

The operation claimed for lead-removal refining includes the treatment of antimony by the mixture of hydroxy acids of phosphorus and sulfuric acid with the nitrogen purge at the antimony melting point. When the hydroxy acids of phosphorus (meta-, ortho-, pyrophosphoric acid) are melting within the mixture of sodium salts, the reaction of phosphates polymerization [3] occurs. As a result, antimony is refined but still contains residual lead of 0.1-0.2%.

Moreover, the mixture of phosphorus pentoxide and sodium carbonate [4] was also experimented with antimony refining at 800 °C, which resulted in the lead decrease down to 0.015% versus its initial content of 4% in the rough metal. The method requires maintaining the ratio of P₂O₅ : Na₂CO₃ = 3:1 and the rate of the refining mixture should be 20% of the metal weight.

Furthermore, the lead-removal reagent [5] is proposed as the mixture containing 30-70% of the reagent with phosphorus oxide, 20-60% sodium phosphate and 2-10% sodium sulfate and/or sodium carbonate and/or sodium phosphate. Metaphosphoric acid and/or polyphosphoric acid and/or phosphoric acid can serve as phosphorus-oxide-containing reagent. In the process of refining with the reagents, the reactions occur with the evolution of H₂O during the decomposition of phosphoric acids (for example, H₃PO₄ → HPO₃ + H₂O), phosphoric salts (for example, NaH₂PO₄ * 2H₂O → NaPO₃ + 3H₂O), as well as with the release of gases. This contributes to the increased losses of antimony with gases.

The current paper reports on the studies carried out for the process of refining antimony with the mixture consisting of sodium dihydrogen phosphate

and phosphoric acid, which intends deep removal of lead and tin from antimony material and decrease in antimony losses with slags and gases.

Experiment description

The reagent for the crude antimony purification from lead and tin was made by preparatory mixing sodium dihydrogen phosphate and phosphoric acid taken in certain ratios. The reagent was dehydrated at the temperature of not lower than 350 °C. The necessary amount of the phosphorus oxide in the mixture ensured the formation of stable phosphates of lead and tin, while the decrease in the sodium content within the mixture allowed the decrease in the antimony losses in the form of antimonate sodium compounds. The refining agent pre-dewatering decreased the evolution of gases during refining and the loss of antimony with gases.

The certain amount of refining reagent or flux was added to 200 g of crude antimony containing 3.46 % of lead and 1.48 % of tin. The mixture was placed in the alundum crucible, heated in a muffle furnace up to 800 °C and held for 30 minutes. After cooling, the refined metal was separated from the slag; both the refined metal and slag were weighed and analyzed in accordance with physical and chemical methods applied to determine the contents of the base metal, lead and tin.

Discussion of the results

When preparing the refining reagent, the ratio of sodium dihydrogen phosphate to the mass of phosphoric acid varied within the range 0.33-1.13. The consumption of the flux to the mass of crude antimony was within the range of 17 - 36.4%. The experimental results have shown (Table 4), that the main factor influencing the degree of antimony refining for lead and tin removal is the composition of the refining mixture, namely the ratio of sodium dihydrogen phosphate to the mass of phosphoric acid. With the increase of this ratio, the degree of antimony purification from lead and tin increased. If the ratio of sodium dihydrogen phosphate to the mass of phosphoric acid was 0.33-0.72, residual lead and tin contents were 0.51-0.012 % and 0.21-0.005 %, respectively. Moreover, when this ratio was of 0.8-1.13, the residual contents of metals were 0.015-0.008 % and 0.005-0.001 %. The table shows the optimum flux consumptions per crude

Table 4. The results of the experiments on antimony refining to remove tin and lead

#	Mass of metal, g		Content, %			Flux flow rate	DHP / <i>acid</i>	Slag mass, g	Sb in slag, %	Alloy yield, %	Extraction of Sb into refined metal, %
			Sb	Pb	Sn						
1	Rough	200	94.48	3.64	1.48	72.8	0.33	65.8	17.93	88.20	92.66
	Refined	176.4	99.26	0.51	0.21						
2	Rough	200	94.48	3.64	1.48	34.0	0.64	50.5	9.80	91.70	97.03
	Refined	183.4	99.97	0.016	0.002						
3	Rough	200	94.48	3.64	1.48	34.0	0.72	50.3	8.75	91.80	97.38
	Refined	183.6	99.97	0.012	0.005						
4	Rough	200	94.25	3.81	1.35	34.0	0.80	50.1	7.70	91.90	97.73
	Refined	183.8	99.97	0.015	0.001						
5	Rough	200	94.09	4.53	1.11	34.0	0.98	49.9	7.17	92.1	97.91
	Refined	184.2	99.97	0.009	0.006						
6	Rough	200	94.09	4.53	1.11	34.0	1.13	49.7	6.64	92.3	98.08
	Refined	184.6	99.98	0.008	0.005						
Note. DHP/acid is the ratio of the weight of dihydrogen phosphate to the mass of phosphoric acid											

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antimony under specified conditions. The increase in flux consumption did not improve the refining parameters, on the contrary, an increased transition of antimony into the slag was observed. Furthermore, the researches have allowed us to determine the optimum conditions for 91.9-92.3 % antimony extraction into the refined metal.

The obtained results have shown the possibility of simultaneous removal of tin and lead from the crude antimony. X-ray phase analysis on the skimmed slags showed the presence of antimony and lead in the form of phosphate compounds, and tin in the form an oxide. In view of the high affinity for oxygen, tin oxidizes at the beginning the process and passes into a slag

phase when refining crude antimony with phosphorus compounds. Lead forms stable phosphorus compounds and is removed from the molten metal, the loss of antimony here is also determined by the formation of antimony phosphates. Under optimal conditions found, the loss of the antimony with the slag phase was between 6 % and 10 %, which could be explained by having formed lead-antimony alloy. The yield of slag was 25-30% of the mass of the rough antimony. The base of the resulting slags was made of phosphorus compounds of sodium (Table 5). The antimony in the resulting slags was extracted by dissolving the latter in water followed by the antimony concentrating in the form of insoluble residue.

Table 5. Refining slag chemical composition analyzed by a microprobe method (%)

Range	O	Na	Al	P	Fe	Sn	Sb	Pb	Total
Range 1	40.16	21.07	0.51	27.45	0.47	0.88	7.06	2.4	100
Range 2	41.19	21.07	0.56	27.12	0.64	0.74	6.91	1.61	100
Range 3	42.04	21.07	0.5	26.90	0.65	0	7.04	1.9	100
Average	41.13	21.04	0.52	27.11	0.59	0.54	6.92	1.97	100.0

Note. All results in weight %

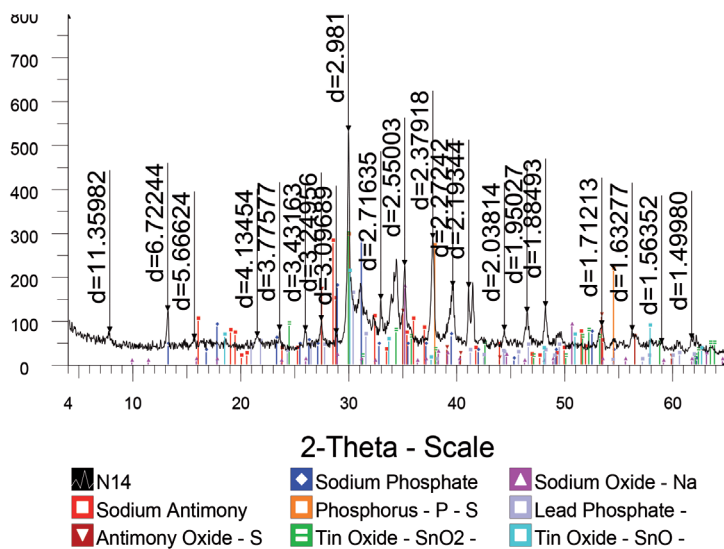


Fig. 1. Diffraction pattern of slag refining

Conclusions

The research has found the optimum composition of the antimony refining mixture for simultaneous removal of lead and tin to the required content. The refining mixture is a reagent obtained by mixing sodium dihydrogen phosphate with phosphoric acid, further dehydrated at 350 °C. The optimum ratio of sodium dihydrogen phosphate to the mass of phosphoric acid is not less than 0.64. The research has achieved optimal refining conditions and the resulting metal contains the residual lead and tin within 0.015-0.008 % and 0.005-0.001 %, against their initial contents of 3.64 % and 1.47 %, respectively.

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