
REMOVAL OF LEAD FROM CRUDE ANTIMONY BY USING NaPO₃ AS LEAD ELIMINATION REAGENT

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Abstract

In order to solve the shortcomings when removing lead from crude antimony in the traditional antimony smelting, a new process was provided using NaPO₃ as lead elimination reagent to yield phosphate slag, and it was removed by floating on the surface of the liquid antimony. Reaction mechanism was clarified by using the TG-DTA and XRD techniques and single factor experiments of removal lead from crude antimony were engaged. The results show that PbO and NaPO₃ begin endothermic reaction at 863K (590°C), and the reaction mainly form NaPb₄(PO₄)₃ and NaPbPO₄ below 1123K (850°C) and above 1123K (850°C), respectively. Sb₂O₃ and NaPO₃ start the reaction at 773K (500°C) and generate an antimonite salt compound. The reaction product of the mixture of PbO, Sb₂O₃ and NaPO₃ show that NaPO₃ reacted with PbO prior when NaPO₃ was insufficient, amorphous antimony glass will be generated only when NaPO₃ was adequate. Single factor experiments were taken with NaNO₃ as oxidizing agent under argon, effect of reaction time, reaction temperature and dosage of NaPO₃ and NaNO₃ on smelting results. The average content of lead in refined antimony was 0.05340% and 98.85% of lead were removed under optimal conditions; the content of lead in antimony have meet the requirements of commercial antimony.

Key words: antimony; Sodium metaphosphate; XRD; Lead elimination reagent; pyro-refining

1 Introduction

China is the largest producer and the vast majority of the reserve base of antimony in the world, accounts for about 80% of the world's mined production^[1-2]. Xikuangshan has been known for a long time as world's antimony capital. The stibnite and jamesonite are two main raw ores for antimony smelting^[2-3], both of them are associated with lead ore^[4]. So the content of lead in crude antimony was from 0.1% to 5%, does not meet the commercial antimony requirements (below 0.2%) and need to be refined.

Hassam V^[5] has studied binary phase diagram of Pb-Sb and confirmed that the maximum solubility of lead in antimony ranged from 1.5 to 2.7 atomic percentage. So separation is difficult owing to the affinity between the two metals. Appropriate

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methods are electrolysis, chloridization, sulfidization and vacuum distillation^[3]. Using sulfidization method to removal of lead are not complete, the lead content can be reduced only to 0.8-1.3%. Chloridization are also noneffective because antimony was easy chlorinated also, this property have been researched by CUI.Y^[6-8] to removal of antimony from liquid copper. Vacuum distillation are not economically viable though it can remove lead complete, and can only be applied to the production of high-purity antimony. Liu Wei-feng^[9] has studied the behavior of lead in selective chlorination leaching process of gold-antimony alloy. Zhang Du-Chao^[10] has researched electrorefining of a gold-bearing antimony alloy in alkaline xylitol solution. All of those are still no industry application. Afterwards, many researchers developed the ammonium salt as lead elimination agent. There are ammonium sulphate ((NH₄)₂SO₄), ammonium phosphate (NH₄)₃PO₄ and ammonium dihydrogen phosphate (NH₄H₂PO₄). This method was effective and lead content can be reduced to 0.1% even less, and it was widely used in antimony fire refining process. But ammonia will pollute the plant and the surrounding environment, the reaction mechanism and products are also unclear, only know it will yield a less density scum. So developing a new environmental friendly lead elimination agent and researching the reaction mechanism have become a urgent problems. In this paper, NaPO₃ was used for lead elimination reagent. NaPO₃ is stable at high temperature and does not cause volatilization of antimony because no water vapor generated. The reaction mechanism was studied by TG-DSC and XRD using pure lead oxide and antimony oxide to react with NaPO₃. Industrial crude antimony was taken as raw materials to carry out conditions experiment for the removal of lead by NaPO₃. The results show that the reaction was completely and the process has no environment contaminate, So NaPO₃ is a clean lead elimination agent. It also can purify other impurity elements in crude antimony.

2 Experimentant

Crude antimony was from Chen-Zhou Mining Group in Hunan province. Table 1 gives the main chemical composition of bullion. As show in Table 1, there was 4.02 wt% of lead and only 94.79 wt % of antimony in sample.

Table 1. The chemical analyses of the crude antimony/(wt.%)

Elements	Sb	Pb	S	Bi	Fe	Cu	Ni	Co	As	Si
Contents	94.79	4.02	0.15	0.01	0.021	0.091	0.034	0.012	0.85	0.023

All reagents were analytical grade. Sodium metaphosphate was obtained by complete dehydration of NaH₂PO₄ • H₂O at 773K (500°C)^[11]. The XRD pattern of synthetic NaPO₃ (JCPDS card, No.11-0648) is shown in Figure 1.

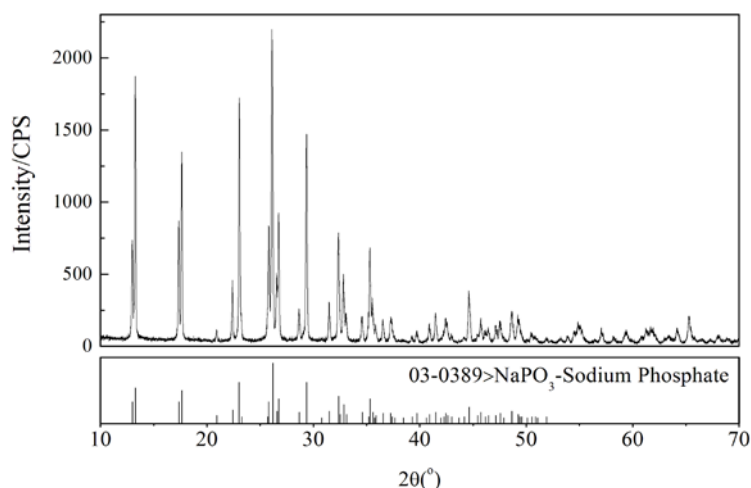


Figure 1. XRD pattern of NaPO_3

Excess of air was bubbled into the furnace to stir and oxidize melt while adding lead eliminatin reagent in industrial production, all of lead was oxidized into PbO . So analytical grade PbO and Sb_2O_3 were used to react with NaPO_3 when taking TG-DSC and XRD analysis to avoid oxidation incomplete. The reaction temperature can be deduced by endothermic and exothermic peak on TG-DSC pattern, then the mixture were charge in an alumina crucible at reaction temperature for 2h for XRD and SEM analysis. Sodium nitrate was added as an oxidant in condition experiments, and ten grams of the metal sample was used every time. The metal and flux samples were charged in an alumina crucible, after the total weight was measure, the crucible with samples was set in the hot zone of the electric furnace, and this moment was defined as the experiment start time. All experiments were carried out with dehydrated high purity argon gas. After the predetermined experimental time, the sample was quenched with flushing argon gas. After the total weight was measured, the metal and flux were separated for chemical analysis. Inductively coupled argon plasma atomic emission spectroscopy was used to analyze the content of Pb in bullion.

X-ray diffraction (XRD) studies were performed using Rigaku D/max 2550VB+18 kw powder diffractometer with a $\text{Cu/K}\alpha$ X-ray source at 40 kV and 300mA. The XRD patterns were recorded with a scan rate of $5^\circ \cdot \text{s}^{-1}$ and a sampling interval of 0.01° . The TG-DSC analysis was performed on a thermogravimetric analyzer of Universal V4.0C TA instrument with SDT Q600 V8.0 Build 95 in a nitrogen flow of 100ml/min and a heating rate of 10 K/min.

The removal ratio of lead (R%) was calculated by the following equation

$$\text{R}\% = \frac{W_1 \cdot x_1\% - W_2 \cdot x_2\%}{W_1 \cdot x_1\%} \times 100\%$$

Where W_1 is the initial mass of crude antimony, g ; W_2 is the mass of refined antimony, g ; x_1 and x_2 are the Pb content in crude and refined antimony respectively.

3 Result and discussion

3.1 Reaction between Sb_2O_3 and NaPO_3

Figure 2 is the TG-DSC result of Sb_2O_3 and NaPO_3 at molar ratio of 1:2. It can

be seen from figure that the quality of the mixture changes little before 800°C. About 3% of total mass was lost because NaPO₃ was easy to absorb water. There are two endothermic peaks between 773K to 873K (500 to 600°C) is may due to endothermic reactions and crystal transition of Sb₂O₃, as we know, cubic antimony trioxide will be transformed into orthorhombic crystal between 823K (550°C) and 850K (577°C)^[12]. Sb₂O₃ evaporate quickly after 1073K (800°C) and NaPO₃ also volatilizes slightly^[13-14], so the total mass was reduced significantly.

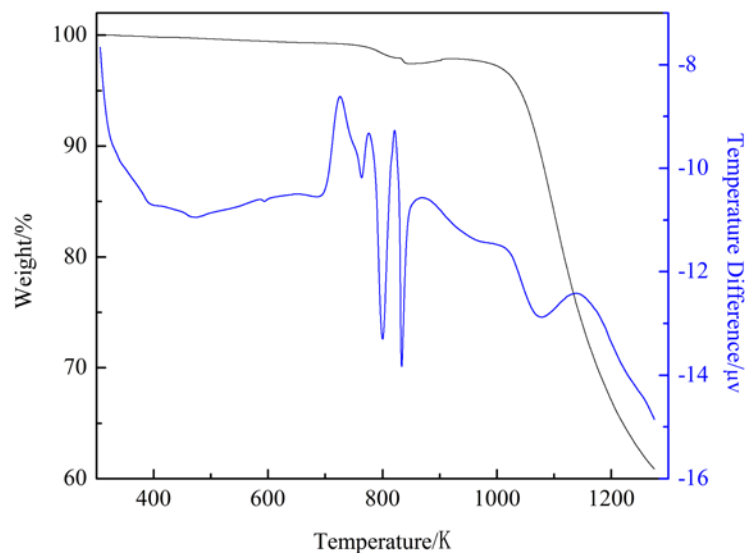


Figure 2. TG-DSC pattern of Sb₂O₃ and NaPO₃ mixture

The XRD patterns of reaction products from the mixture of Sb₂O₃ and NaPO₃ calcined at the different temperatures are shown in Figure 3. Comparing the XRD patterns to the JCPDS files, it illustrates that all the peaks of the samples are identified as antimony trioxide (JCPDS card, No.42-1466) at 673K (400°C), which meaning NaPO₃ and Sb₂O₃ didn't react. SbPO₄(JCPDS card, No.35-0829) was generated when temperature was high than 773K (500°C). The product become amorphous when the temperature was high than 923K (650°C) because NaPO₃ melted and generated a glassy compound with Sb₂O₃^[15].

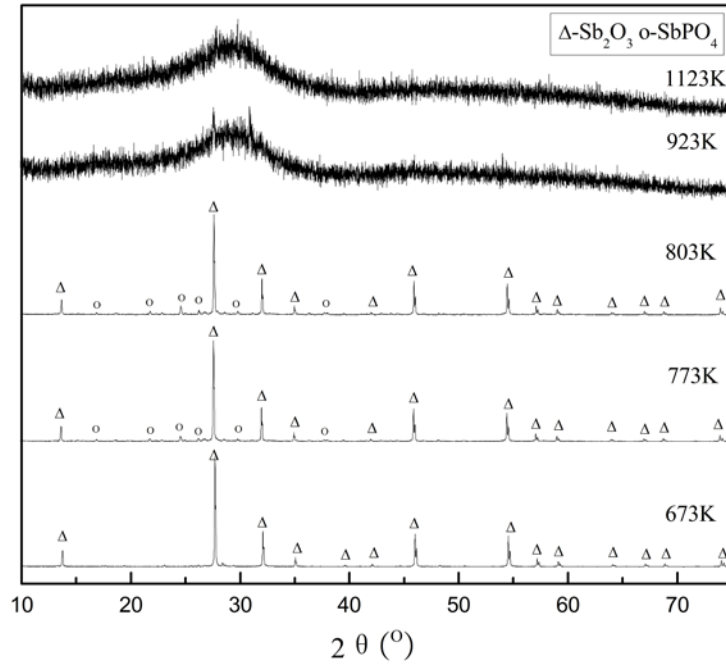


Figure 3. XRD patterns of Sb_2O_3 and $NaPO_3$ mixture at different temperature (a)-803K;(b)-923K;(c)-1123K

Possible reactions in this process were as fellow^[16-17]:

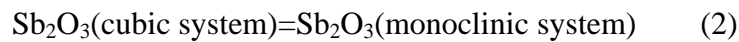
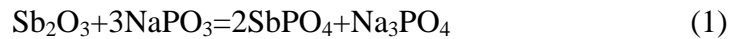


Figure 4 shows the SEM micrographs of the reaction products of Sb_2O_3 and $NaPO_3$ at different temperatures, it can be seen from the figure that the sample at 803K (530°C) were smaller irregular grains, it should be just a mixture of Sb_2O_3 and $NaPO_3$. The mixture became large particles as the temperature increased. The particles of uniform morphology and size were yield at 1123K (850°C).

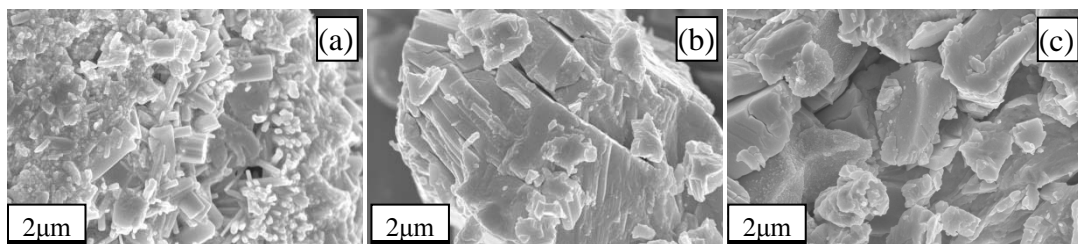


Figure 4. SEM images of Sb_2O_3 and $NaPO_3$ mixture at different temperature (a)-803K;(b)-923K;(c)-1123K

3.2 Reaction between PbO and $NaPO_3$

The results of TG-DSC pattern of PbO and $NaPO_3$ at the molar ratio of 1:1 are shown in Figure 5. We can see from the pattern that about 3.5% of the total mass was lost before 673K (400°C), it was due to the removal of adsorbed water and bounded water from the mixture. The quality was almost constant during 673K (400°C) to 1073K (800°C), but there were four distinct endothermic and exothermic peaks,

indicating there were physical or chemical reaction taken place. The largely mass loss was caused by the volatilization of PbO after 1073K (800°C).

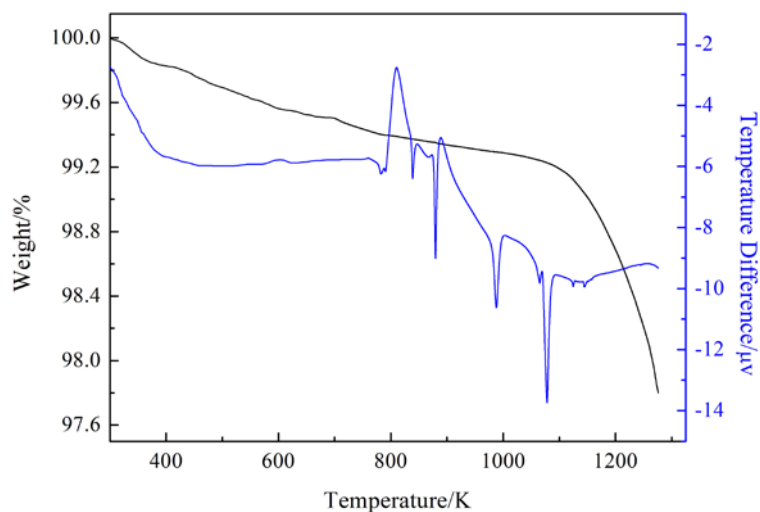


Figure 5. TG-DSC pattern of PbO and NaPO₃

Figure 6 show the XRD patterns of reaction products from PbO and NaPO₃ calcined at the different temperatures. It can be seen that all the peaks before 773K (500°C) are identified as PbO (JCPDS card, No.38-1477, No.05-0561) and NaPO₃ (JCPDS card, No.11-0648) indicated there were no reaction between NaPO₃ and PbO. The patterns of the products have the same shape at 863K (590°C), 923K (650°C) and 1023K (750°C), included NaPb₄(PO₄)₃ (JCPDS card, No.29-1230), Pb₃(PO₄)₂ (JCPDS card, No.03-0677) and NaPbPO₄ (JCPDS card, No.36-0342), but mainly generated NaPbPO₄ at 1123K (850°C) and the peaks of NaPb₄(PO₄)₃ were decreased. It indicated that NaPbPO₄ was more stable under high temperature. The peaks of PbO disappeared at 1123K (850°C) showed the reaction between PbO and NaPO₃ was complete.

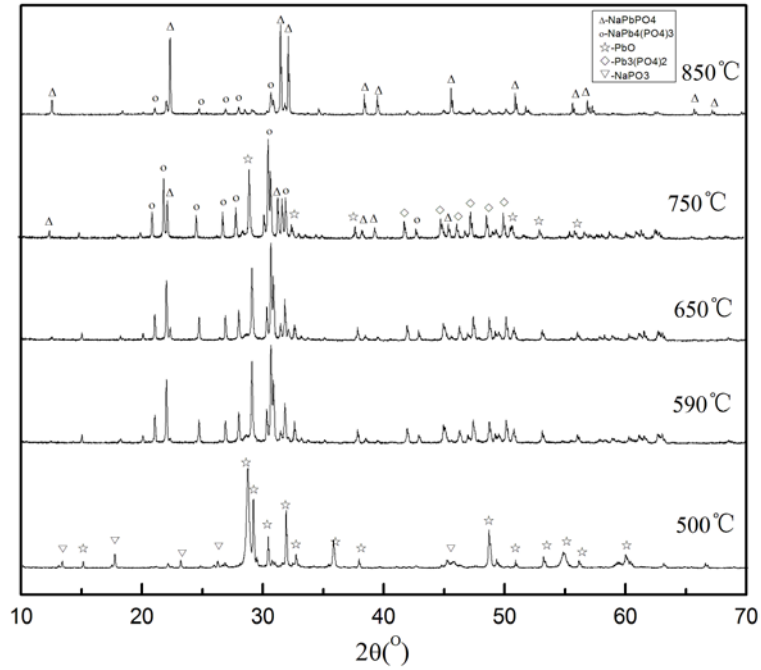
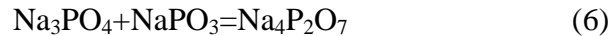
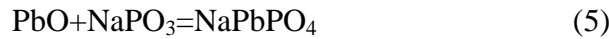
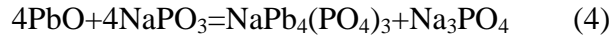


Figure 6. XRD patterns of PbO and NaPO₃ at different temperature (a)-923K;(b)-1023K;(c)-1123K

Relevant possible reactions were as follow:



The SEM images of products at different temperatures are exhibited in Figure 7. It can be seen from the figure that there were small and diluted particles at 923K (650°C). When temperature rise to 1123K (850°C), larger amount of compact particles were formed, indicated the reaction were completed fully.

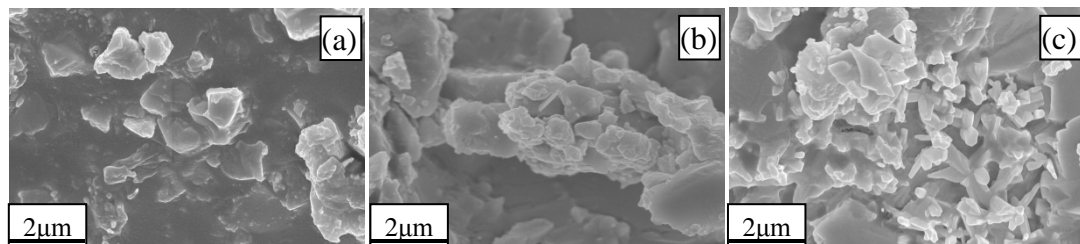


Figure7. SEM images of PbO and NaPO₃ at different temperature(a)-923K;(b)-1023K;(c)-1123K

3.3 Reaction between PbO, Sb₂O₃ and NaPO₃ mixture

The mixture of different molar ratio of PbO, Sb₂O₃ and NaPO₃ were reacted at 1123K (850°C) for 2h, and the XRD patterns of reaction products were shown in

figure 8. When the molar ratio of PbO: Sb₂O₃: NaPO₃ was 2:1:2, that was mean the amount of NaPO₃ was insufficient to react with both, NaPbPO₄ was yielded and Sb₂O₃ were still oxide meaning that meaning NaPO₃ combined with PbO firstly. As the amount of NaPO₃ increasing, PbO generated NaPbPO₄ yet, but Sb₂O₃ phase disappeared because of synthetic reaction, so PbO combines NaPO₃ prior.

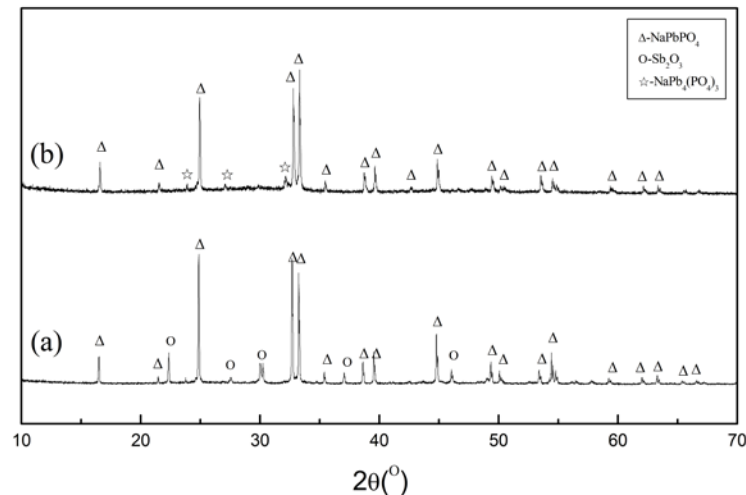


Figure 8. XRD patterns of Sb₂O₃, PbO and NaPO₃ at different molar ratio (a) PbO: Sb₂O₃: NaPO₃=2: 1: 2; (b) PbO: Sb₂O₃: NaPO₃=2: 1: 4;

3.4 Condition Experiments

The factors influencing the content of lead in refined metal and removal ratio of lead were studied under experimental conditions including reaction time and temperature, dosage of NaPO₃ and NaNO₃.

3.4.1 Effect of duration

The effect of reaction was investigated in the range from 5 to 90 min, at temperature 1073k (800°C), dosage of NaPO₃ and NaNO₃ at 6g and 0.3g respectively. The relationship between lead content in antimony, removal ratio of lead and treatment time are shown in Figure 9a.

As shown in Figure 9a, within 20 min, the lead content in antimony decreased gradually as the duration was increased. For an decrease in time from 5min to 20 min, the Pb% decreased from 0.2451% to 0.178%. After the duration of 20min, prolonging the reaction time will result in content increase, which may caused by diffusion of lead and volatilize of antimony. The removal ratio remained constant hardly as time increased in whole process.

3.4.2 Effect of NaPO₃ dosage

The effect of NaPO₃ dosage was investigated in the range from 10% to 100% of the crude antimony mass, treatment time at 20min, at temperature 1073K (800°C) and the dosage of NaNO₃ was as much as last time. The relationship between refining result and NaPO₃ dosage are shown in Figure 9b.

As shown in Figure 9b, the content of Pb in metal decrease from 1.7609% to 0.07761% when the NaPO₃ dosage from 10% to 60%. Nevertheless, the Pb% increases a little with the growth of NaPO₃ dosage when the dosage was over 60%.

It can be explained that viscosity of melt was increase and it was difficult to layer, because the viscosity of melting NaPO_3 is very large. On the other hand, the volatilization loss of antimony was grown due to less residues and insufficient to coverage of the metal when NaPO_3 dosage is little.

3.4.3 Effect of NaNO_3 dosage

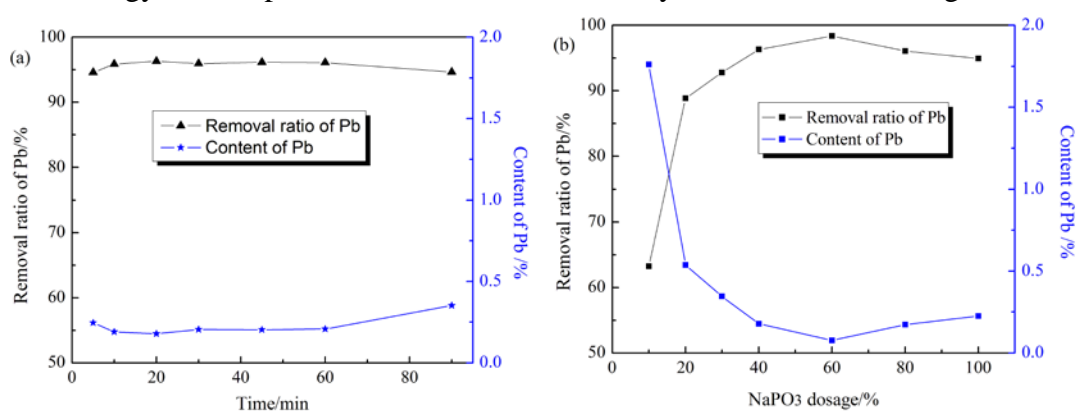
The effect of NaNO_3 dosage on the Pb% and R% was investigated in the range from 1 to 6 wt%, NaPO_3 dosage at 60% and experiments were carried out at 1073K (800°C) for 20 min. The experimental results are shown in Figure 9c.

As shown in Figure 9c, within 3% NaNO_3 , the content of Pb decreased gradually as the NaNO_3 dosage was increased. For an increase in dosage from 1% to 3%, the Pb% decreased from 0.1145% to 0.07761%. When the NaNO_3 dosage was more than 3%, the Pb% gradually increase with increasing the NaNO_3 dosage, because increasing the NaNO_3 dosage causes the amount of Na_2O increase from the thermal decomposition of NaNO_3 and an increase of the oxidation of antimony, both of them will also consume NaPO_3 dosage.

3.4.4 Effect of reaction temperature

The effect of reaction temperature on the Pb% and R% was investigated in the range from 973 to 1173K (700 to 900°C), NaPO_3 and NaNO_3 dosage at 60% and 3% respectively, and experiments were carried out for 20 min. The experimental results are shown in Figure 9d.

As can be seen from Figure 9d, the content of lead in bullion decrease obviously as the temperature was increased. When the temperature increase from 973 to 1023K (700 to 750°C), the removal ratio percent correspondingly decrease from 0.231% to 0.05283%. This can be explained by the fact that the kinetics increase and viscosity of flux decrease as the temperature was increased. The content of lead and removal ratio were almost constant while the temperature was more than 1073K (800°C). After the reaction temperature of 1073K (800°C), prolonging the temperature will result in more energy consumption and volatilize of antimony, which comes to naught.



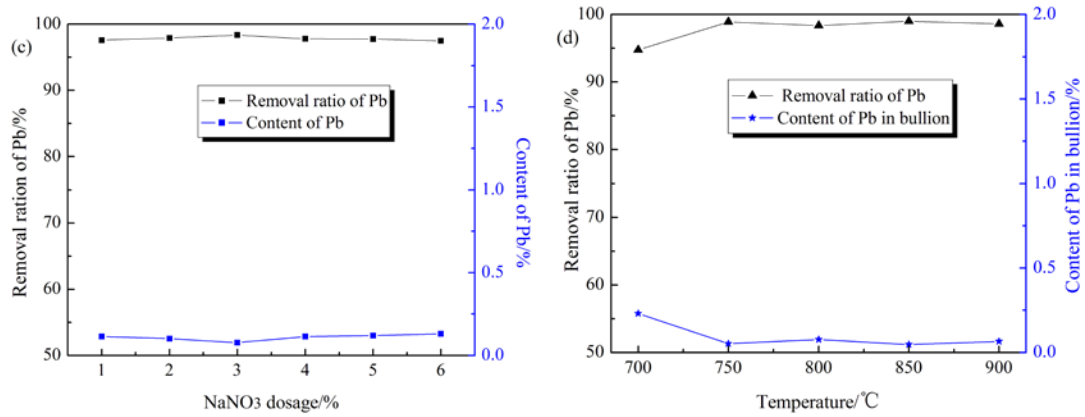


Figure 9. Effects of (a) reaction time, (b) dosage of NaPO_3 , (c) dosage of NaNO_3 , (d) reaction temperature on removal ratio of lead and content of lead in bullion

3.5 Comprehensive Experiment

Comprehensive experiments were carried out for three times under optimum conditions, reaction temperature at 1023K (750°C) for 20 min, dosage of NaPO_3 and NaNO_3 at 60% and 3%, respectively, the results are shown in Table 2.

Table 2. Result of comprehensive experiment/%

No	Content of Pb before refining	Content of Pb after refining	Removal ratio
1	4.02	0.05283	98.90
2	4.02	0.05048	98.93
3	4.02	0.05690	98.71
Average	4.02	0.05340	98.85

It can be seen from the table the average content of lead was 0.05340%, which had met the commercial antimony requirements. The average removal rate of lead was 98.85%, lead removal process was complete. The complete analysis for antimony under the optimum conditions was taken by ICP-AES and the purification ability of NaPO_3 to other impurity metals was investigated, the result is shown in Figure 10.

It can be seen from the figure that NaPO_3 has an excellent purifying effects to major impurity elements involved Pb, S, Fe, Co, Si, but the selective binding ability was poor for Bi, Cu, Ni. It also suggested that NaPO_3 can be applied as lead elimination reagent in the refining process of these metals.

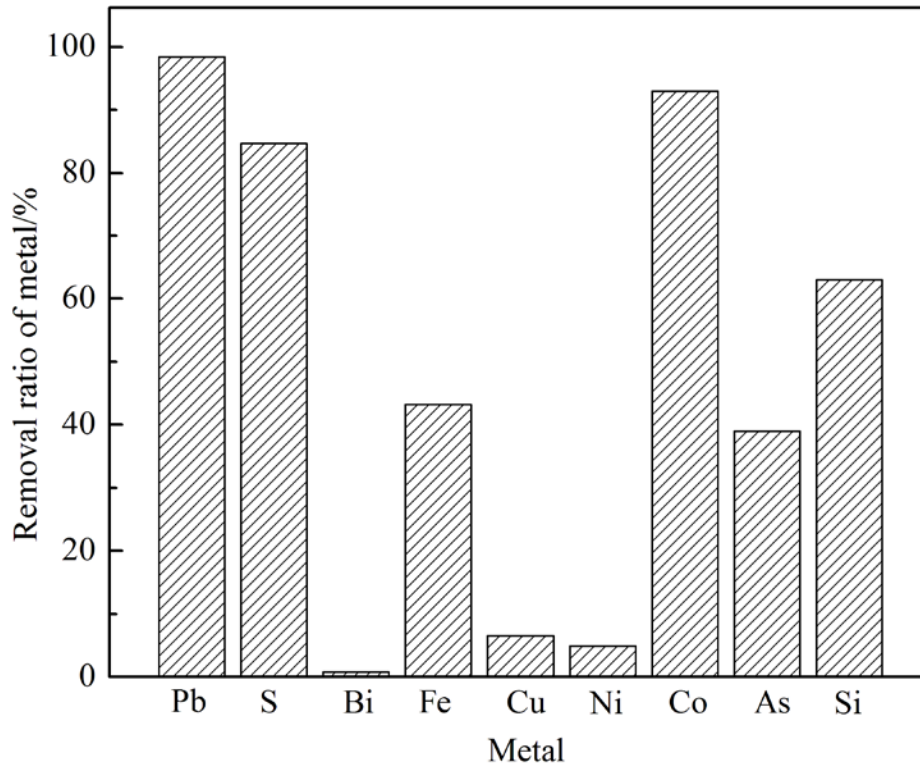


Figure 10. Removal ratio of various impurity metals in the refining process

4 Conclusions

In this study, the reaction mechanism of NaPO_3 used as lead elimination reagent for crude antimony refining was studied by TG-DTA and XRD. The results show that PbO and NaPO_3 begin reaction at 863K (590°C), mainly formed $\text{NaPb}_4(\text{PO}_4)_3$ and NaPbPO_4 when below 1123K (850°C) and above 1123K (850°C) respectively. Sb_2O_3 and NaPO_3 start the reaction at 773K (500°C) and yield an amorphous antimony vitreous compound. The reaction product of mixture of PbO , Sb_2O_3 and NaPO_3 show that NaPO_3 priority reacted with PbO when NaPO_3 was insufficient, amorphous antimony glass will be generated when enough NaPO_3 was existed. The optimum conditions of refining process was reaction temperature at 1023K (750°C) for 20 min, dosage of NaPO_3 and NaNO_3 at 60% and 3% respectively. The content of lead in refined antimony was 0.05340% and 98.85% of lead were removed under optimal conditions, meet the requirements of commercial antimony. The reaction process was environmentally friendly. To sum up, NaPO_3 is a cleaning and highly effective lead elimination agent.

Acknowledgements

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Figures list

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Figure10 Removal ratio of various impurity metals in the refining process

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