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REMOVAL OF LEAD FROM CRUDE ANTIMONY BY USING $NaPO_3$ AS LEAD ELIMINATION REAGENT

L.G. Ye, C.B. Tang*, S.H. Yang, Y.M. Chen, W.H. Zhang

Central South University, School of Metallurgy and Enviroment, Hunan, China

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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 $NaPO_3$ 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 $NaPO_3$ begin endothermic reaction at 863K (590°C), and the reaction mainly form $NaPb_4(PO_4)_3$ and $NaPbPO_4$ below 1123K (850°C) and above 1123K (850°C), respectively. Sb_2O_3 and $NaPO_3$ start the reaction at 773K (500°C) and generate an antimonic salt compound. The reaction product of the mixture of PbO, Sb_2O_3 and $NaPO_3$ show that $NaPO_3$ reacted with PbO prior when $NaPO_3$ was insufficient, amorphous antimony glass will be generated only when $NaPO_3$ was adequate. Single factor experiments were taken with $NaNO_3$ as oxidizing agent under argon, effect of reaction time, reaction temperature and dosage of $NaPO_3$ and $NaNO_3$ 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.

Keywords: 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 [3-4], both of them are associated with lead ore [5]. 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 [6] 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 [7]. Appropriate methods are electrolysis, chloridization, sulfidization and vacuum distillation [4]. 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 [8-9] 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 [10] has studied the behavior of lead in selective chlorination leaching process of gold-antimony alloy. Zhang Du-Chao [11] 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 ($(NH_4)_2SO_4$)), ammonium phosphate $(NH_4)_3PO_4$ and ammonium dihydrogen phosphate ($NH_4H_2PO_4$). 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, $NaPO_3$ was used for lead elimination reagent. $NaPO_3$ is stable at high

* *Corresponding author: tangchaobo9043@163.com*

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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 $NaPO_3$. Industrial crude antimony was taken as raw materials to carry out conditions experiment for the removal of lead by $NaPO_3$. The results show that the reaction was completely and the process has no environment contaminate, So $NaPO_3$ is a clean lead elimination agent. It also can purify other impurity elements in crude antimony.

2. Experimental

Crude antimony was from Chen-Zhou Mining Group in Hunan province. Table 1 gives the main chemical composition of the 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 $NaH_2PO_4 \cdot H_2O$ at 773K (500°C) [12]. The XRD pattern of synthetic $NaPO_3$ (JCPDS card, No.11-0648) is shown in Figure 1.

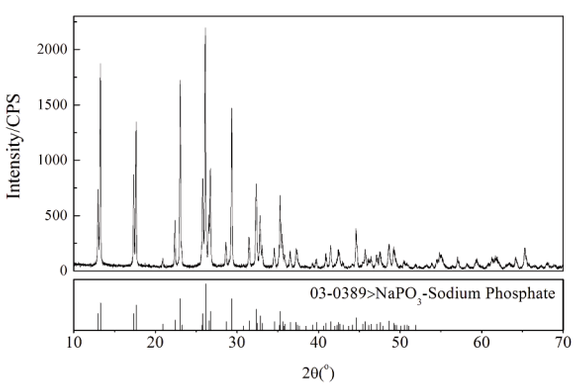

Figure 1. *XRD pattern of $NaPO_3$*

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 peaks 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 measured, 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 Cu/Kα X-ray source at 40 kV and 300mA. The XRD patterns were recorded with a scan rate of $5^{o} \cdot s^{-1}$ and a sampling interval of 0.01^{o}. 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

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

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 $NaPO_3$ 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 Sb_2O_3, as we know, cubic antimony trioxide will be transformed into orthorhombic crystal between 823K (550°C) and 850K (577°C) [13]. Sb_2O_3 evaporate quickly after 1073K (800°C) and $NaPO_3$ also volatilizes slightly [14-15], so the total mass was reduced significantly.

The XRD patterns of reaction products from the mixture of Sb_2O_3 and $NaPO_3$ 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),

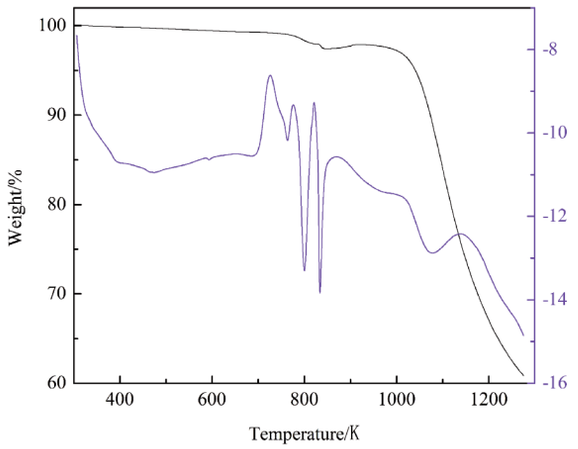

Figure 2. *TG-DSC pattern of Sb_2O_3 and $NaPO_3$ mixture*

which meaning $NaPO_3$ and Sb_2O_3 didn't react. $SbPO_4$(JCPDS card, No.35-0829) was generated when temperature was high than 773K (500ºC). The product become amorphous when the temperature was high than 923K (650ºC) because $NaPO_3$ melted and generated a glassy compound with Sb_2O_3 [16].

Possible reactions in this process were as fellow [17-18]:

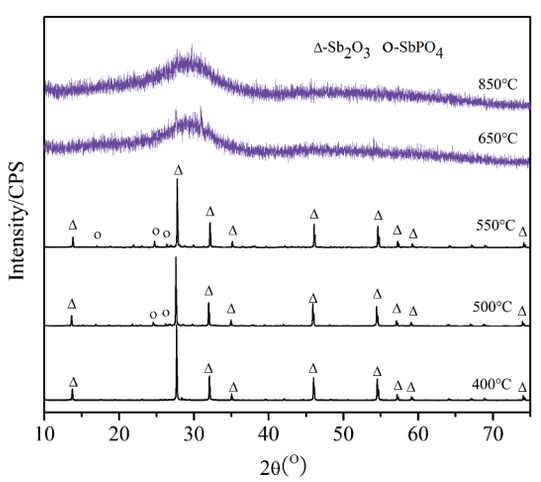

Figure 3. *XRD patterns of Sb_2O_3 and $NaPO_3$ mixture at different temperature (a)-803K;(b)-923K;(c)-1123K*

$$Sb_2O_3+3NaPO_3=2SbPO_4+Na_3PO_4 \quad (1)$$

$$Sb_2O_3(\text{cubic system})=Sb_2O_3(\text{monoclinic system}) \quad (2)$$

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 (530ºC) was 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 (850ºC).

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 (400ºC), it was due to the removal of adsorbed water and bounded water from the mixture. The quality was almost constant during 673K (400ºC) to 1073K (800ºC), 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 (800ºC).

Figure 6 show the XRD patterns of reaction products from PbO and $NaPO_3$ calcined at the different temperatures. It can be seen that all the peaks before 773K (500ºC) are identified as PbO (JCPDS card, No.38-1477, No.05-0561) and $NaPO_3$ (JCPDS

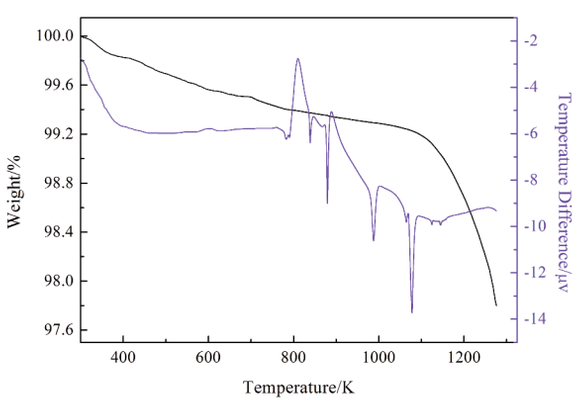

Figure 5. *TG-DSC pattern of PbO and $NaPO_3$*

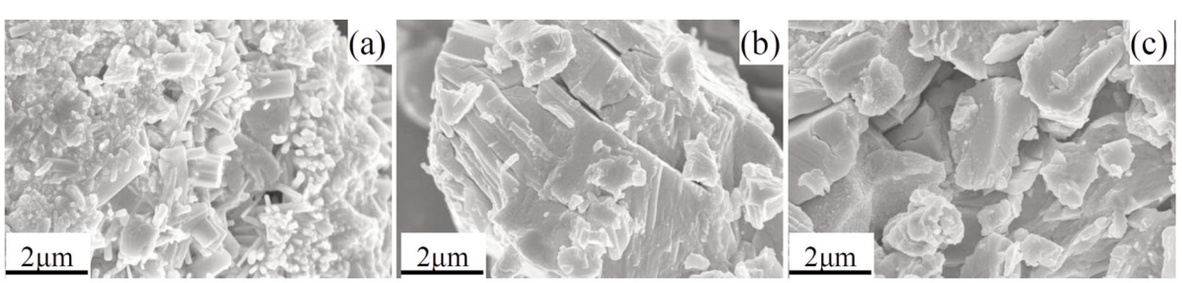

Figure 4. *SEM images of Sb_2O_3 and $NaPO_3$ mixture at different temperature (a)-803K;(b)-923K;(c)-1123K*

card, No.11-0648) indicated there were no reaction between $NaPO_3$ and PbO. The patterns of the products have the same shape at 863K (590°C), 923K (650°C) and 1023K (750°C), included $NaPb_4(PO_4)_3$ (JCPDS card, No.29-1230), $Pb_3(PO_4)_2$ (JCPDS card, No.03-0677) and $NaPbPO_4$ (JCPDS card, No.36-0342), but mainly generated $NaPbPO_4$ at 1123K (850°C) and the peaks of $NaPb_4(PO_4)_3$ were decreased. It indicated that $NaPbPO_4$ was more stable under high temperature. The peaks of PbO disappeared at 1123K (850°C) showed the reaction between PbO and $NaPO_3$ was complete.

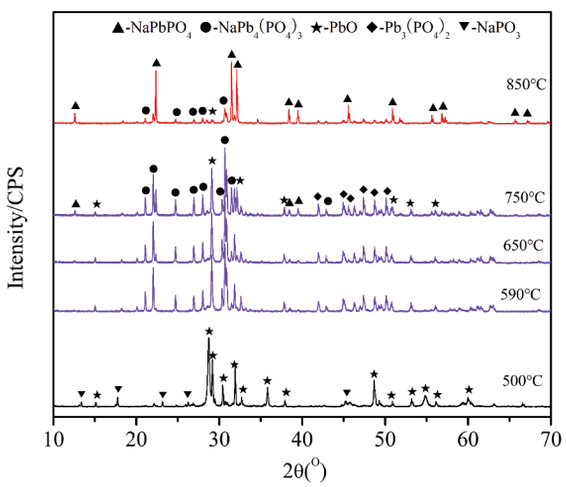

Figure 6. *XRD patterns of PbO and $NaPO_3$ at different temperature (a)-923K;(b)-1023K;(c)-1123K*

Relevant possible reactions were as fellow:

$$3PbO+3NaPO_3=Pb_3(PO_4)_2+Na_3PO_4 \quad (3)$$

$$4PbO+4NaPO_3=NaPb_4(PO_4)_3+Na_3PO_4 \quad (4)$$

$$PbO+NaPO_3=NaPbPO_4 \quad (5)$$

$$Na_3PO_4+NaPO_3=Na_4P_2O_7 \quad (6)$$

The SEM images of products at different temperatures are exihibited 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.

3.3 Reaction between PbO, Sb_2O_3 and $NaPO_3$ mixture

The mixture of different molar ratio of PbO, Sb_2O_3 and $NaPO_3$ 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: Sb_2O_3: $NaPO_3$ was 2:1:2, that was mean the amount of $NaPO_3$ was insufficient to react with both, $NaPbPO_4$ was yielded and Sb_2O_3 were still oxide meaning that meaning $NaPO_3$ combined with PbO firstly. As the amount of $NaPO_3$ increasing, PbO generated $NaPbPO_4$ yet, but Sb_2O_3 phase disappeared because of synthetic reaction, so PbO combines $NaPO_3$ prior.

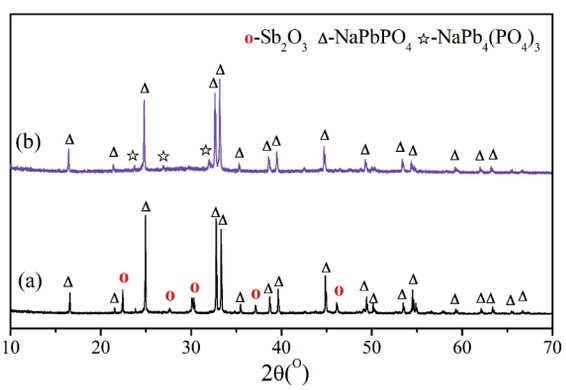

Figure 8.*XRD patterns of Sb_2O_3, PbO and $NaPO_3$ at different molar ratio(a) PbO:Sb_2O_3: $NaPO_3$= 2:1 :2; (b) PbO:Sb_2O_3:$NaPO_3$=2:1:4;*

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 $NaPO_3$ and $NaNO_3$.

3.4.1 Effect of duration

The effect of reaction time was investigated in the

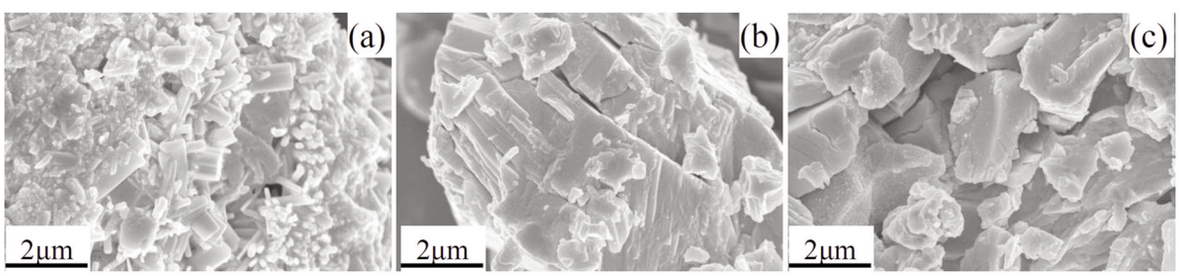

Figure7. *SEM images of PbO and $NaPO_3$ at different temperature(a)-923K;(b)-1023K;(c)-1123K*

range from 5 to 90 min, at temperature 1073k (800°C), dosage of $NaPO_3$ and $NaNO_3$ 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 $NaPO_3$ dosage

The effect of $NaPO_3$ 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 $NaNO_3$ was as much as last time. The relationship between refining result and $NaPO_3$ 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 $NaPO_3$ dosage from 10% to 60%. Nevertheless, the Pb% increases a little with the growth of $NaPO_3$ 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

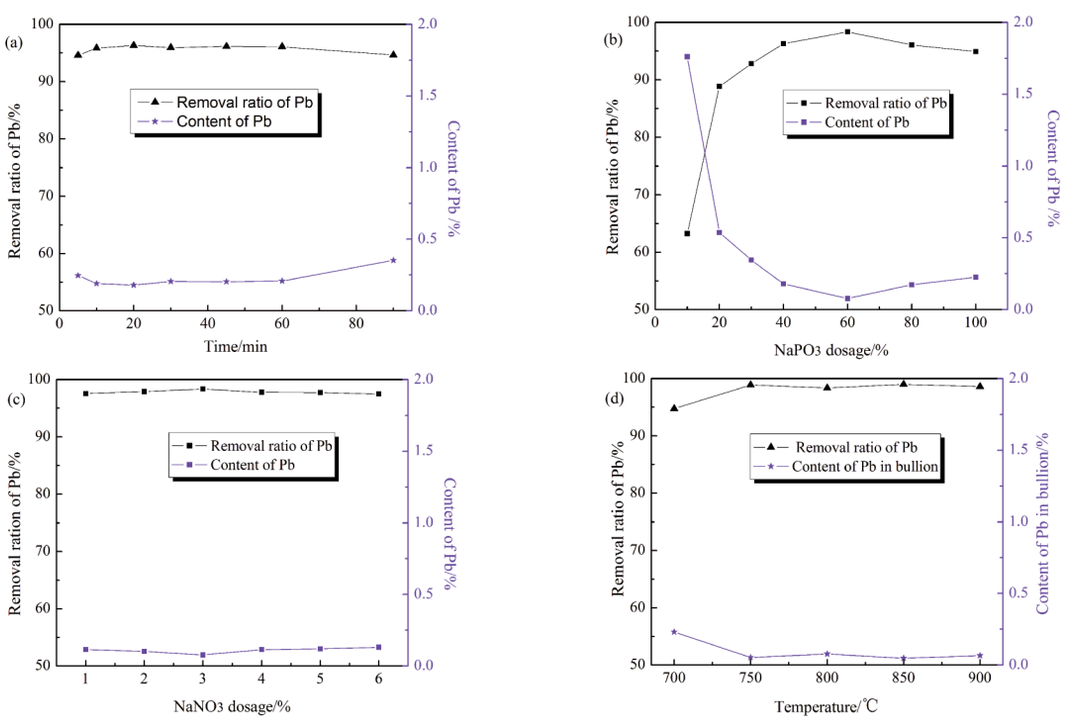

Figure 9. *Effects of (a) reaction time, (b) dosage of $NaPO_3$, (c) dosage of $NaNO_3$, (d) reaction temperature on removal ratio of lead and content of lead in bullion*

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.

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. *Ressult of comprehensive experiment/%*

No	Content of Pb before refining	Content of Pb after refining	Removal ratio
1	4.02	0.05283	98.9
2	4.02	0.05048	98.93
3	4.02	0.0569	98.71
Average	4.02	0.0534	98.85

It can be seen from the table the average content of lead was 0.05340%, which had meet 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.

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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 $NaPb_4(PO_4)_3$ and $NaPbPO_4$ when below 1123K (850°C) and above 1123K (850°C) respectively. Sb_2O_3 and $NaPO_3$ start

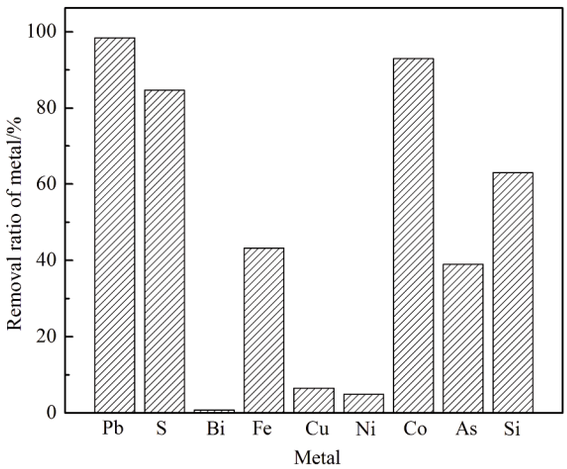

Figure10. *Removal ratio of various impurity metals in the refining process*

the reaction at 773K (500°C) and yield an amorphous antimony vitreous compound. The reaction products 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 existted. 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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