

## **Method Article**

### **Antimony Removal by Sodium Nitrate in Lead Purification Process**

**Abstract** - The modified Harris Process which uses sodium carbonate and sodium nitrate is currently being used to remove antimony during the lead purification process in the battery manufacturing process. This study investigates the possibility of using sodium nitrate alone to remove antimony from lead. The process was carried out in a lead-purifying kettle. The optimum temperatures used were in the range of 600 – 650 °C. Turnaround time was reduced from 24 hours to 16 hours. Yield was increased from 67% to 78%. The purity of the lead obtained was 99.9% analysed by Atomic Absorption Spectroscopy which is ideal in the battery manufacturing. The results indicate that sodium nitrate can be used alone as a cost-effective method for the removal of antimony.

**Key words:** Lead, antimony, sodium nitrate, Harris process.

## **1. INTRODUCTION**

Lead (Pb) is the backbone of the lead acid battery manufacturing process. Pure lead is the main raw material required for the production of lead acid batteries. It is used for the production of positive and negative electrodes paste. The specification of pure lead required for battery manufacturing is as follows (Vinal ,1996).

Pb = 99.95 % min

Antimony (Sb) = 0.005 % max

Copper (Cu) = 0.005 % max

Arsenic (As) = 0.0005 % max

Tin (Sn) = 0.001 % max

Iron (Fe) = 0.001 % max

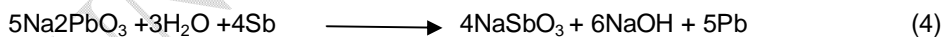
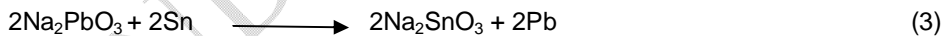
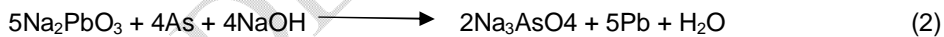
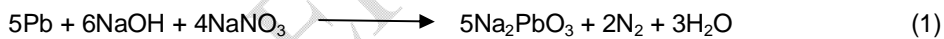
Bismuth (Bi) = 0.01 % max

Lead from battery scrap produced in a secondary lead smelter contains a different levels of alloying elements (S, Cu, Ni, As, Sb, Bi, Ag, Au, etc.). The research gets antimony as reference point because

of its bad effect on battery electrical conductivity characteristics. Different purification processes have been employed which include Betts electrolytic refining, vacuum distillation and pyro-metallurgical refining process (Harris). The Betts electrolytic refining uses an electrical cell, the process cannot be implemented at industrial scale due to the high cost of electrolysis (Liddel, 1945). Vacuum Distillation is a complicated technique long in its flow sheet and low in metal recovery and non economical (Siegmund, 2010).

### Pyro-Metallurgical Refining Process (Harris)

The Harris method is a method for refining the liquid **bullion in which the bullion is sprayed through molten caustic soda and molten sodium nitrate at 450°C. Then arsenic**, antimony and tin are oxidized, converted into sodium salts and skimmed from the bath. "The first step involves **the removal of Copper** and the second step involves the removal of Antimony, **Arsenic and Tin. The removal of copper is done by sulfurization of copper. A skim from copper sulphide will float at** the surface of the molten lead and can be skimmed off. The 2<sup>nd</sup> step is a batch process (oxidation process) done by gradually adding powder of sodium nitrate (50 kg) into the molten vortex followed by adding sodium hydroxide flake (25 kg) to agglomerate the dross, a flux of bubble air flowing through the molten with efficient mixing. The oxidation process(cycle) takes about 1.5 hours" ( Jones, 1929). Theoretically a complex reaction occurs during this process forming salts compound as follows (scribd.com/doc/30131781/Lead-and Lead-Iloys).



This process has proved to be costly **as two chemicals are used during** the treatments.

The modified Harris process uses sodium carbonate instead of sodium hydroxide and sodium nitrate. This process has proved to be costly as lead recoveries averages 67% against a target of 80% causing a significant cost in under recoveries. The cycle time is unstable, and the

process is marked by high turnaround times and high chemical usage as two chemicals are used. This makes the process unsustainable. In order to increase yield and lower the turnaround times the alternative is to separate lead and antimony at higher temperatures between 600°C and 650°C which can be maintained in the pot as for the Harris process as shown phase diagram in Figure 1 with the use of fewer reagents.

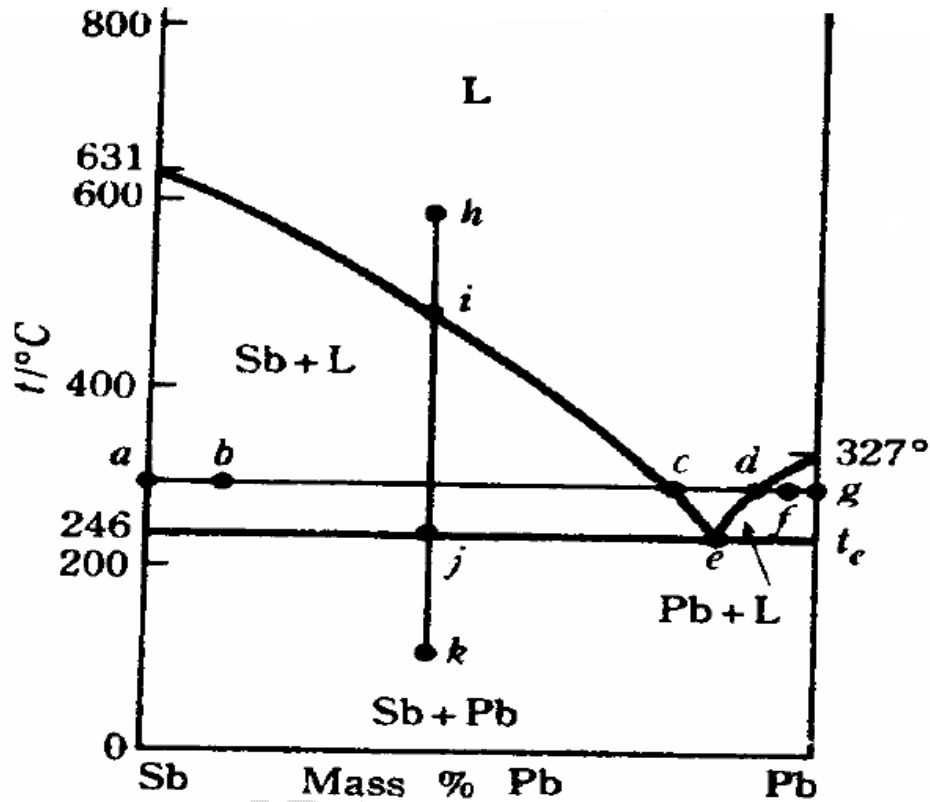


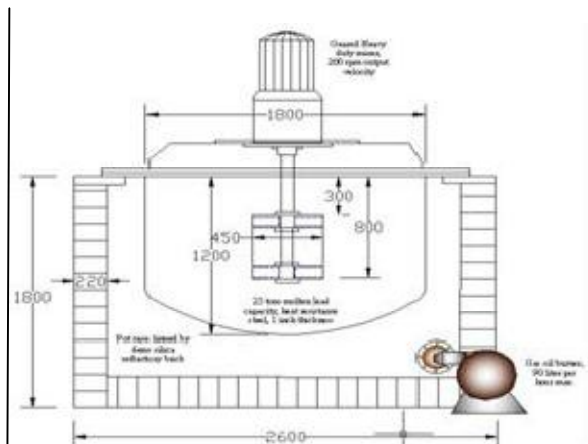
Figure 1 Lead antimony phase diagram (source Hassam *et al.*, 2009)

The main objective of this work was to investigate the possibility of using sodium nitrate alone instead of sodium nitrate and sodium carbonate to remove antimony from battery lead scrap in a lead refining kettle.

## 2. Materials and Method

### 2.1. Materials

Lead Kettle 20-ton capacity as shown in Fig.2 complete with refractory lined case, mixer and self-proportional oil burner was used. Molten lead electrical pump 10 tons per hour capacity. AAS for laboratory routine chemical analysis for detection of impurities concentration in molten lead were used.



**Figure 2. 20 ton lead kettle complete with refractory lined case, burner and mixer [7].**

### Experimental Objectives

1. Determining the quantity of sodium nitrate required to purify one batch cycle and compare with the quantities of sodium nitrate and sodium carbonate used in the Harris process
2. Determining the amount of dross removed.
3. Determining the process time for each batch.
4. Evaluating the feasibility of the sodium nitrate process and making comparison with the Harris process

### Experimental Procedure

1. Charge the 20 tons pot by the rotary furnace crude lead bullion for melting.
2. Skim the slag from the molten surface.
3. Add saw dust with a shovel to facilitate the drying of the cleaning dross.
4. When the dross is dry and the pot temperature is at a minimum of 500°C, clear off the dross and take a sample for initial analysis of antimony, copper and antimony
5. Add sulphur at the molten vortex to remove cooper sulphide skim from the molten surface.

### Experimental Design

1. Adjust temperatures to between 600°C and 650°C.
2. Slowly add 25kgs of sodium nitrate placed at the edge of the pot and stir for 30 minutes or until when the dross turns orange with red spots.

3. Add another 25kgs of sodium nitrate and continue stirring for another 30 minutes with the temperature maintained between 600°C and 650°C.
4. Remove the dross and take a sample for analysis.
5. Repeat steps 1 to 4 until antimony is within specification requirements.

### 3. Results and Discussion

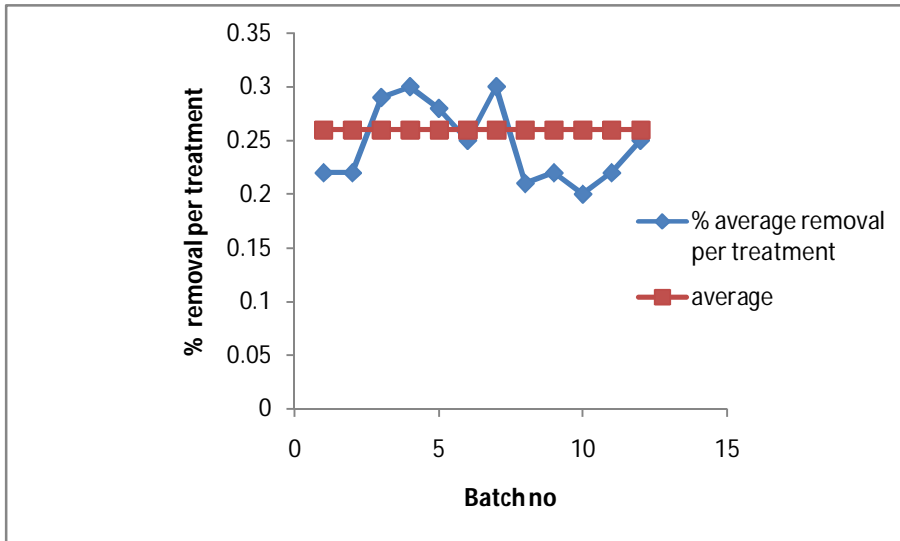
#### Experimental Results

Table1: Shows the results obtained by using sodium nitrate in the removal of antimony from crude lead to produce high purity lead to be used in battery manufacturing for twelve batches

**Table 1. Experimental results of using sodium nitrate in the removal of antimony from crude lead**

Batch no	Crude Input kgs	Cleaning Dross kgs	Cu dross kgs	Initial Sb%	No of removals	% average removed per treatment	Sb Usage kgs	NaNO <sub>3</sub> Usage kgs	Output Purified lead kgs	Time (h)	% Recovery
1	18684	1919	728	1.3	6	0.22	300	14165	18	75.81	
2	19603	1860	834	1.2	5.5	0.22	275	14926	17	76.14	
3	20658	1676	650	1.19	4	0.29	200	16832	14	81.48	
4	18283	745	577	1.17	4	0.30	200	14302	14	78.23	
5	19180	3603	100	1.1	4	0.28	200	12946	13	67.50	
6	20253	1500	356	1.02	4	0.25	250	16709	14	82.50	
7	18283	745	577	1.17	4	0.30	200	14302	14	78.23	
8	18930	1000	532	0.85	4	0.21	220	13837	14	81.48	
9	17843	1430	142	0.8	3.5	0.22	160	14260	13	79.92	
10	20207	2000	239	0.7	3.5	0.20	175	16918	13	83.72	
11	20123	1770	701	0.65	3	0.22	150	15949	13	79.26	
12	19316	1688	110	0.62	2.5	0.25	125	15663	12	81.09	
<b>Ave</b>						0.26127	206		14	78	

**Average antimony removal per treatment per batch by using Sodium Nitrate**

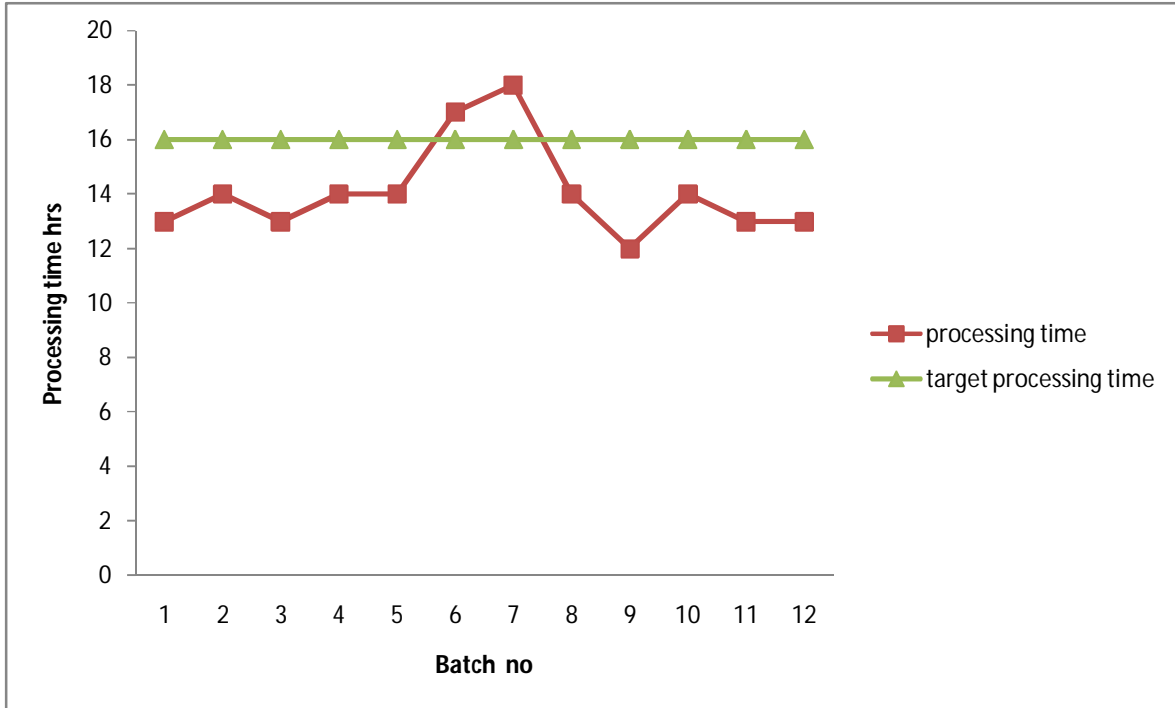


**Figure 3. Average antimony removal per treatment per batch by using Sodium Nitrate**

Figure 3 shows the efficiency and effectiveness of removals by monitoring the average antimony reduction by the number of treatments per treatment per batch by using sodium nitrate.

The average percentage removal increased from 0.16 % for the Harris process to 0.25 % for the Sodium Nitrate process. Hence indicating that sodium nitrate is more efficient than the combination of sodium hydroxide and sodium nitrate used in the Harris process.

### Processing Time

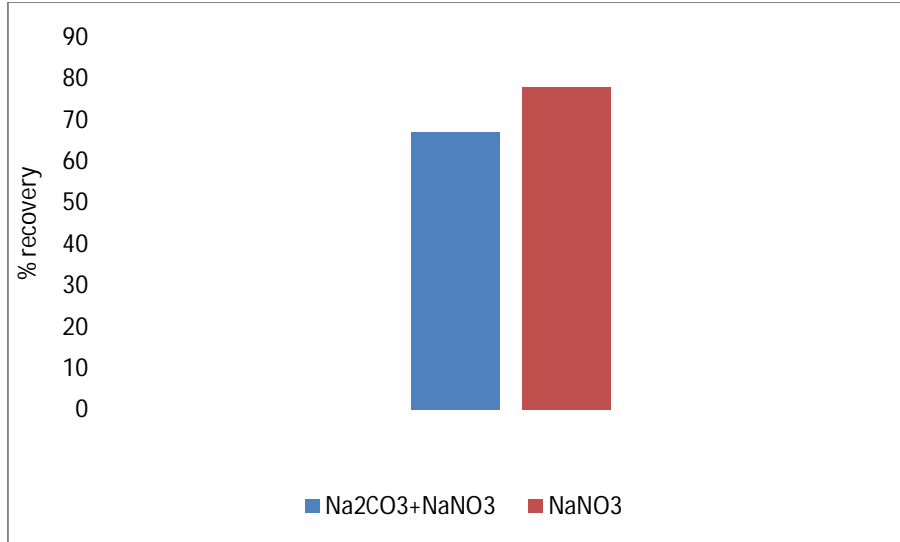


**Figure 4. Turnaround time for pure lead processing**

The average time taken for processing the pots reduced from 24 to 16 hours, 83 % of the pots processed were completed within 16 hours. This resulted in overall processing cost reduction of \$0.17 per kg of processed lead from \$1.82 to \$1.65 per kg. Average monthly pure output is 60 tones and this will translate to \$10200 savings per month.

### Feasibility Evaluation

**Recovery:** Figure 5 shows average recovery of lead from batches treated with  $\text{Na}_2\text{CO}_3$  and  $\text{NaNO}_3$  with batches treated with  $\text{NaNO}_3$  alone.



**Figure 5 Recovery comparison of  $\text{Na}_2\text{CO}_3+\text{NaNO}_3$  vs.  $\text{NaNO}_3$**

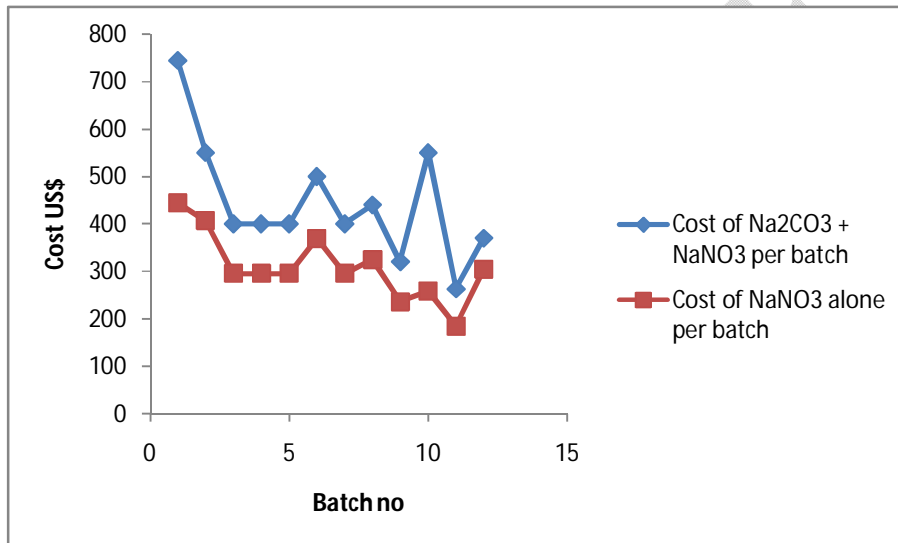
Recovery significantly improved from 67 to 78 %. This resulted in increased productivity within the smelter and increase in pots yield. The increase in recoveries resulted in a decrease in processing cost from \$1.55 to \$1.40 per kg of processed lead hence \$ 0.15 will be realized from every kilogram of processed lead. Monthly savings will be \$9000.

### Cost benefit of Sodium Carbonate plus Sodium Nitrate versus Sodium Nitrate

Table 2 and figure 6 shows the Cost benefit analysis of Sodium Carbonate plus Sodium Nitrate versus Sodium Nitrate alone.

**Table 2. Cost benefit of Sodium Carbonate plus Sodium Nitrate versus Sodium Nitrate**

Batch no	Cost of Na <sub>2</sub> CO <sub>3</sub> + NaNO <sub>3</sub> per batch US\$	Cost of NaNO <sub>3</sub> alone per batch US\$
1	744	444
2	550	407
3	400	296
4	400	296
5	400	296
6	500	370
7	400	296
8	440	325.6
9	320	236.8
10	550	259
11	263	185
12	369.88	304.8
Average	444.74	309.69



**Fig 6 Cost benefit analysis of Sodium Carbonate plus Sodium Nitrate versus Sodium Nitrate alone.**

From Table 2, a cost benefit of (US\$444.74- US\$309.69) US\$135.05 will be achieved batch.

Monthly savings per month from four batches will be US\$540.16.

Overall cost savings per month will be US\$19740.16 and US\$236 881.92 per year.

## Conclusions

The results obtained from the experiments indicate that it is possible to use sodium nitrate alone to remove antimony from crude lead. Use of sodium nitrate results in increase in recoveries from 68% to 78% and decrease in turnaround time from 24 to 16 hours. This results in increase in the overall performance and output of the smelter and achievement in cost savings.

## References

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