Modified pyro-metallurgical technology for recovery of impurities from crude lead using chalk powder

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Abstract

Harris process is a well-known technology for purification of lead from alloying elements (impurities) antimony, tin and arsenic, this process use sodium nitrate as an oxidizing agent. Sodium nitrate is not enough secure to be used in a foundry because its composition contains easily liberated oxygen for continuous burning even without the existence of environmental oxygen. This is on one side and on the other side sodium nitrate has limited availability because it can be used in the manufacturing of explosive material. The scope of the research is to find a material which can substitute for sodium nitrate and be feasible, safe and has no environmental impact. The Harris method used sodium nitrate as an oxidizing agent with sodium hydroxide for agglomeration of the floated skim over molten lead followed by the bubbling of air through the molten lead which is done under controlled temperatures and with efficient mixing.

It is found from the research that the fine powder of calcium carbonate grain (chalk powder) takes a role as an oxidizing agent without air bubbling. It is shown that the oxidation reactions occur on the surface of calcium carbonate granules, is yellow–brown skims floating over molten surface from impurities and lead oxidant, whenever a fine grain used, a higher efficiency is achieved. The new technology has many advantages but it has also disadvantages represented by increasing process technology time by 15% and increasing the amount of solid skimmed waste by 10% which can later be recycled again to the

rotary furnace for reduction getting high antimony lead which is preferable for the production of an electrode grid for a lead acid battery.
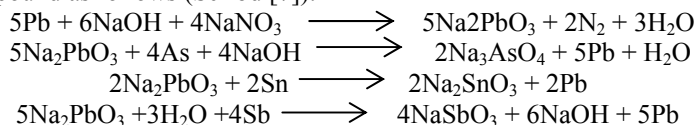
Keywords: purification of lead.

1   Introduction

Pure lead is the main raw material in the manufacturing of lead acid batteries, where it used in the manufacturing of positive and negative electrodes paste. The lead purity should not be less than 99.95%. The standard specification of pure lead is as follows (Vinal [1]):

Lead content   =   99.95% min
(Sb) Antimony =   0.005% max
(Cu) Copper   =   0.005% max
(As) Arsenic   =   0.0005% max
(Sn) Tin   =   0.001% max
(Fe) Iron   =   0.001% max
(Bi) Bismuth   =   0.01% max

Pure lead produced in secondary lead smelter from battery scrap which contains different level of alloying elements (S, Cu, Ni, As, Sb, Bi, Ag, Au, etc.), purification of lead in this research means mainly removing antimony Sb, arsenic As and tin Sn by oxidation process. The research gets antimony as reference point because of its bad effect on battery electrical characteristics. The lead is reduced from battery scrap in a rotary furnace to produce crude lead bullion. The pyro-metallurgical purification process start when that leads bullion melts in a 20 tons kettle capacity for refining process from remaining slag and alloying elements by pyro-metallurgical refining process (Environment Agency [2], lead-smelting.html [3] and Jones [4]).

1.1 Pyro-metallurgical refining process (Harris)

The first step is to remove copper and the second step is to remove antimony, arsenic and tin. The removal of copper is done by sulfurization of copper. A skim from copper sulfide will float at the surface of the molten lead and can be skimmed off. The second 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 takes about 1.5 hours (Cycle), Pinson [5], ILA [6] Jones [4]). Theoretically a complex reaction occurs during this process forming a salts compound as follows (Scribd [7]):

$$5Pb + 6NaOH + 4NaNO_3 \longrightarrow 5Na2PbO_3 + 2N_2 + 3H_2O$$
$$5Na_2PbO_3 + 4As + 4NaOH \longrightarrow 2Na_3AsO_4 + 5Pb + H_2O$$
$$2Na_2PbO_3 + 2Sn \longrightarrow 2Na_2SnO_3 + 2Pb$$
$$5Na_2PbO_3 + 3H_2O + 4Sb \longrightarrow 4NaSbO_3 + 6NaOH + 5Pb$$

1.2 Electrolytic refining

This is done by Betts Process using electrical cell, the cathode electrode is free copper raw lead sheet while the anode is a thin sheet of pure lead. The electrolyte used is a fluosilicate acid (H_2SiF_6). When electrical DC current switched on, the lead at the cathode slowly dissolves and deposited as a highly purity clusters upon the anode (Burroughs [8], Bray [9] and Liddell [10]).

1.3 Sodium nitrate ($NaNO_3$)

Sodium nitrate is a strong oxidizing agent used in the Harris process. It reacts violently with flammables, combustibles, many organic compounds, metals granulated or powdered (aluminium, magnesium), often causing fires and explosions. When reacted with strong acids, it forms toxic nitrogen dioxide.

2 The choice of alternative oxidizing material

The selection of another oxidizing material is limited by three factors:
1. Should be safe handling and storage.
2. Low price and feasible.
3. Available here in Iraq and easy to prepare.

So first we look to the other approximately similar structures and it is found that calcium carbonate has the same chemical formula but different chemical specifications. It is stable and has no chemical activities until the temperature is increased to 950ºC. It is a common substance found in rock with the chemical formula $CaCO_3$. Sometimes calcium carbonate is used in the metallurgical process for physical effect. It helps to separate slag from metal in furnaces. Calcium carbonate is widely used as an extender in paints, filler and in construction materials.

Amorphous calcium carbonate (ACC) is an important type for oxidation reactions because it has a large interfacial surface area for reaction so it has high activity for reactions. And that activity will increase with increasing temperature, reducing grain size (d) and increasing void fraction, so according to these facts we designed a program of experiments to determine the ability of available $CaCO_3$ grains (50 micron) for the oxidation process and separated elements from lead. The specifications of available calcium carbonate used in this research is:

Synthesis grade $CaCO_3$ purity > 95%; Sieve analysis < 100 micron.

3 Equipment used in the research

1. Lead Kettle 20 ton capacity (fig. 1), complete with refractory lined case, mixer and self-proportional oil burner.
2. Molten lead electrical pump, 10 tons per hour capacity.
3. Laboratory routine chemical analysis for detection of impurities concentration (concn.) in molten.
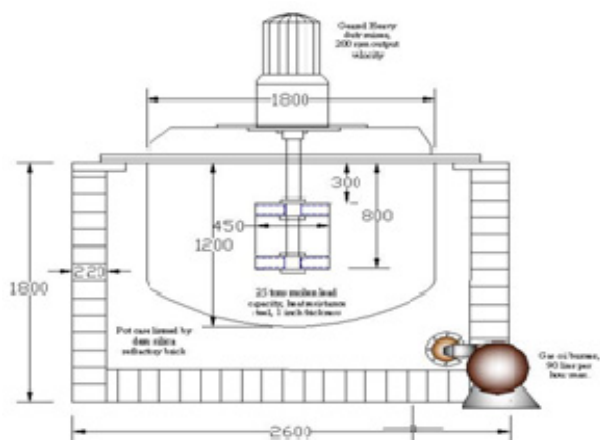
Figure 1:   20 ton lead kettle complete with refractory lined case, burner and mixer.

4   The topics of the research

1. Study the primary effect of calcium carbonate grain on removing elements.
2. Study the effect of the initial concn. of antimony on process efficiency.
3. Determine the quantity of calcium carbonate used to purify one batch cycle and compared with the incidence of sodium nitrate used for the same purpose.
4. Determine the amount of dross removed.
5. Determine the technological process time for each batch.
6. Calculate the feasibility study of the two methods and make comparison.

5   The experimental procedure steps

1. Charge the 20 ton pot by the rotary furnace crude lead bullion for melting.
2. Skim slag from the molten surface.
3. Add sulfur at the molten vortex for removing cooper sulfide skim from the molten surface.
4. Remove antimony by adding fine powder of calcium carbonate at the molten vortex at different temperature and cycle time. With continuous mixing for 45 min. for each cycle then skim the dross.

6   The experiment's design

1. At different initial concn. of antimony determine the quantity of sodium nitrate and sodium hydroxide needed for purification at constant temperature, using a flux of 500 cm^3 bubble air through the media.
2. At different initial antimony concn., determine the quantity of calcium carbonate and sodium hydroxide needed for purification at constant temperature.

3. At constant initial antimony concn., determine the rate of decreasing antimony concn. related to purification cycles for the two processes.
4. At constant initial antimony concn., determine the amount of dross removed for the two processes.
5. Determine the effect of calcium carbonate grain size on the purification efficiency.

7 The experimental results

Table 1 shows the results from 10 experiments according to 6.1. The amount of oxidizing agents in Kg for the Harris process with different initial antimony concn. for ten experiments.

Table 1:   Results from 10 experiments according to 6.1.

Exp. No	Initial concn. of antimony	Total amount of sodium nitrate Kg	Total amount of sodium hydroxide Kg	Process time hours
1	2.10	450	250	12
2	1.88	400	200	11
3	1.85	400	200	10
4	1.80	350	175	10
5	1.73	350	200	12
6	1.70	400	200	10
7	1.27	400	200	12
8	1.15	300	150	8
9	1.10	350	200	8
10	0.48	150	100	4

Table 2 shows the results from 10 experiments according to 6.2. The amount of calcium carbonate and sodium hydroxide in Kg with different initial antimony concn. for ten experiments.

Table 2:   Results from 10 experiments according to 6.2.

Exp. No	Initial antimony concn.	Total amount of calcium carbonate Kg	Total amount of sodium hydroxide Kg	Process time hours
1	1.91	450	225	14
2	1.76	450	225	13
3	1.50	400	200	12
4	1.40	350	175	11
5	0.94	300	150	10
6	0.91	300	150	10
7	0.85	275	125	9
8	0.73	225	100	8
9	0.60	175	75	7
10	0.51	150	75	6

Table 3 shows the results from 9 experiments according to 6.3. The decrease of antimony concn. for each process cycles (Harris and calcium carbonate) at the same initial antimony concn. and constant operating temperature.

Table 3:   Results from 9 experiments according to 6.3.

Process cycle number	% Sb for Harris technology	% Sb for CaCO$_3$ method
1	2.20	2.20
2	1.75	1.85
3	1.45	1.55
4	1.1	1.30
5	0.75	1.05
6	0.5	0.8
7	0.2	0.5
8	0.05	0.2
9	0.01	0.05

Table 4 shows the results from 9 experiments according to 6.4. The amount of skimmed dross for Harris and calcium carbonate at the same initial antimony concentration and constant operating temperature.

Table 4:   Results from 9 experiments according to 6.4.

Initial antimony concentration	Harris total dross Kg	CaCO3 total dross Kg
2.10	4000	4400
1.88	3800	4100
1.80	3600	4000
1.73	3450	3900
1.70	3400	3900
1.27	3000	3300
1.15	2900	3200
1.10	2900	3200
0.48	2100	2400

Table 5 shows the results from 5 experiments according to 6.5. The effect of calcium carbonate grain size on the reduce antimony for single cycle.

Table 5:   Results from 5 experiments according to 6.5.

Grain size	Average concn. of antimony reduced in the cycle (Δ Sb %)
50	0.5
100	0.35
200	0.2
500	0.02
1000	0.01

8   Discussions of the results

For the Harris method, fig. 2 shows the relation between the amount of sodium nitrate and sodium hydroxide in Kg (oxidizing agents) with different initial concn. of antimony. It takes a straight line.

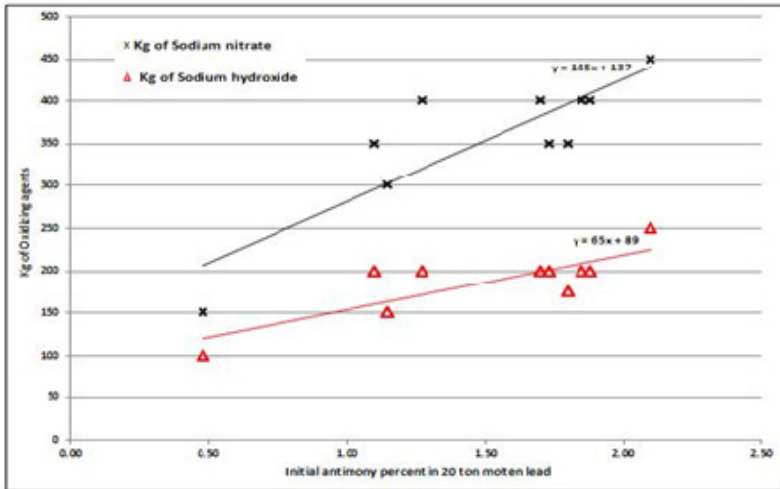$Y1 = YNaNO_3 = 145$ X (initial antimony concn.) $+ 137$
$Y2 = YNaOH = 65$ X $+ 89$

Figure 2:   The amount of sodium nitrate and sodium hydroxide in Kg with different initial conc. of antimony for the Harris method.

For the calcium carbonate method, fig. 3 shows the relation between the amount of calcium carbonate and sodium hydroxide in Kg with different initial concn. of antimony. The relations take a straight line model.

$Y1 = YCaCO_3 = 209$ X (initial antimony percent) $+ 75$
$Y2 = YNaOH = 111$ X $+ 27$

Figure 4 shows the comparison between Harris technology and the calcium carbonate method relating to the increasing of total process time with increasing initial antimony concn.. The relation takes a straight line model, and shows the time needed for Harris process is lower than that for $CaCO_3$ by about two hours.

Figure 5 shows the comparison between the efficiency of the Harris method and that using $CaCO_3$ at a constant initial concn. of antimony 2.25 %, related to decrease antimony for each cycle. It is shown that the Harris process has better efficiency than $CaCO_3$ and goes faster and the rate increase for high concn. of antimony while it is a straight line for $CaCO_3$.
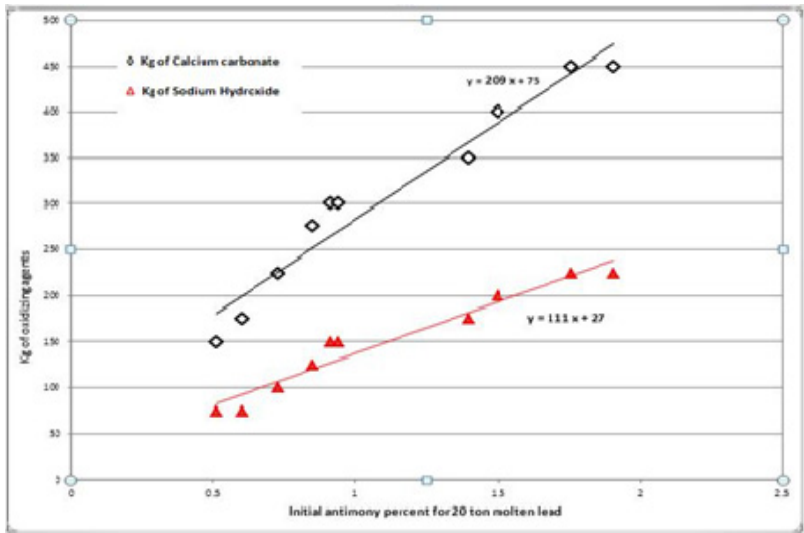
Figure 3:   The amount of calcium carbonate and sodium hydroxide in Kg
             with different initial concn. of antimony.

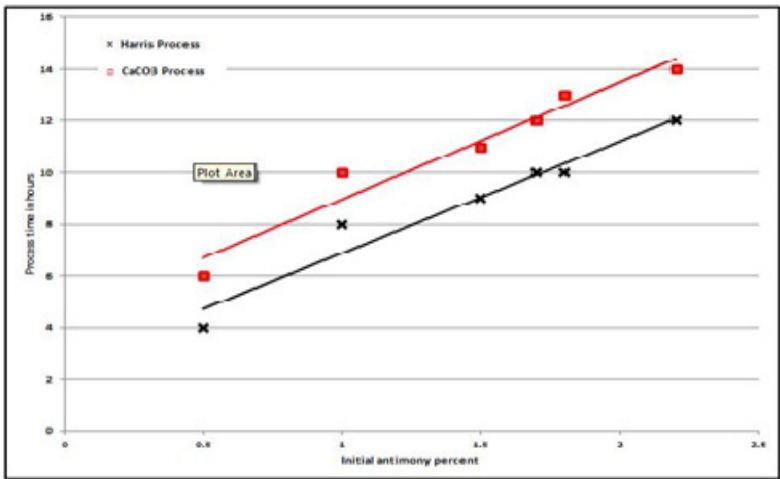
Figure 4:   The comparison between the efficiency of the Harris method and
             CaCO₃ related to the total process time.

Figure 6 shows the total amount of dross skimmed for the Harris process
compared with calcium carbonate for different initial antimony concn. Normally
the dross amount reduced as the initial antimony concn. reduced and takes a
straight line shape. The difference seems to be constant 500 kg, antimony lead
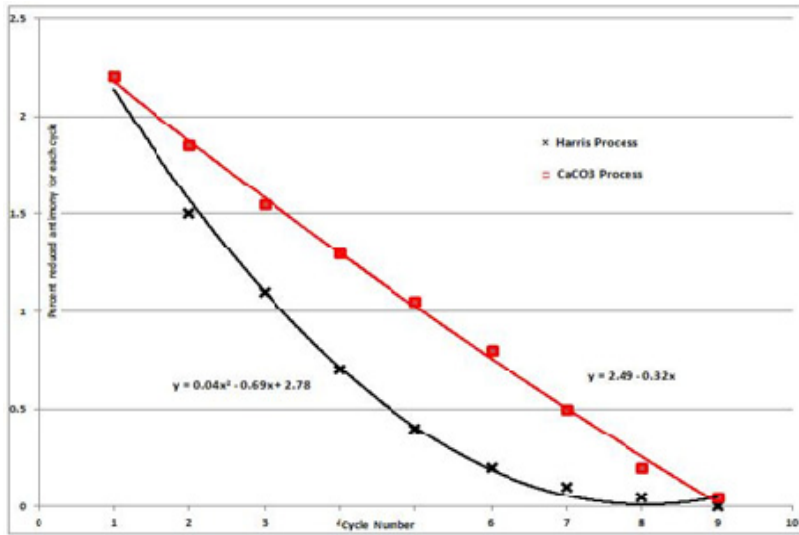will extract later from that dross in the rotary furnace.

Figure 5:   The comparison between the efficiency of the Harris method and
              CaCO$_3$ at a constant initial concn. of antimony 2.25% related to
              reduce antimony for each cycle.
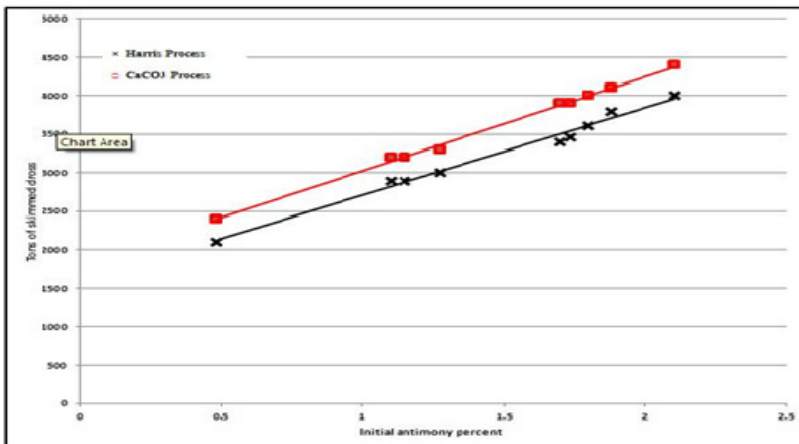

Figure 6:   The comparison between the Harris process and CaCO$_3$ related to
              the total amount of skimmed dross at different initial antimony
              concn.

Table 5 shows the positive effect of fine calcium carbonate grain size on the
efficiency of calcium carbonate method. It is shown that a particle size less than
100 micron of calcium carbonate give suitable results but for 500 micron it
becomes useless.

It has been observed from experiments that the calcium carbonate grain surface colour changes from white to yellow – brown which means that a layer of mainly oxidized lead build up over the grain. The chemical analyses show that this layer contains impurities oxides (COSQC [13]).

9 Feasibility overview

9.1 Losses

Table 6 shows a comparison between the two processes related to the amount of materials consumed, dross removed (charged again to rotary furnace for reduction of high antimony lead) and process time (number of cycles) for 20 ton molten lead, 2% initial antimony purification.

Table 6:   Comparison between the two processes.

Item	Harris Process	$CaCO_3$ Process
Oxidizing agents (Kg)	450 $NaNO_3$	500 $CaCO_3$
Sodium Hydroxide (Kg)	250	250
Total dross skimmed (Kg)	3800	4300
Number of cycles (80 min. for each cycle)	8 (11 hours)	9 (13 hours)
Production of pure lead (Kg)	16200	15800

9.2 Profit

The price of one ton sodium nitrate commercial grade reach Iraq about 800$, while the price of one ton calcium carbonate is about 100 $ and it is available locally, lead dross will reduced in the rotary furnace to produce high antimony lead with small loses not more than 10%, so the negative effect of difference in dross amount is neglected, the cost of the operation time of one cycle more for $CaCO_3$ (two hours) about 50 $ (labor, equipment depreciation and services).

The positive cost for $CaCO_3$ in $ = cost of sodium nitrate for 2% initial antimony 20 ton lead purification – cost of calcium carbonate – cost of technological time + cost of safety (not evaluated) = 360 – 50 – 50 + safety = 260$ + Safety to use for a production of 16 ton of pure lead (99.97), so for one ton = 16.2$ + safety. Safety means easy to handle, no firing problem and locally available without security problem.

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