PERFORMANCE EVALUATION OF LEAD RECOVERY PLANT.
(A CASE STUDY OF WEST AFRICAN BATTERIES LIMITED, IBADAN.)

BY

SADIQ S. OVAKACHI
92/2682

CHEMICAL ENGINEERING DEPARTMENT, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA.

DECEMBER 1998.

DECLARATION

I Sadiq S. Ovakachi declare that this project work is purely my work and to the best of my knowledge has never being presented elsewhere either in part or wholly for the award of any degree or diploma.
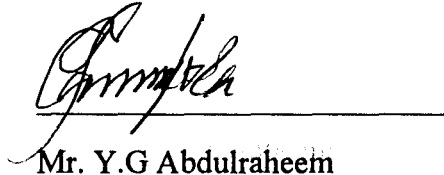
-----------------   ------------------

SIGNATURE   **DATE**

CERTIFICATION

I Certify that this project titled, "Performance Evaluation of Lead Recovery Plant."
(A case study of West African Batteries Ltd.) was carried out by Sadiq S.O., under the
supervision of Mr Y.G Abdulraheem of Department of Chemical Engineering Federal
University of Technology, Minna.

_____   _15ᵗʰ Dec. 1995_

Mr. Y.G Abdulraheem   Date

Project Supervisor

_____   _____

Dr. J.O Odigure   Date

Head of Department

_____   _____

External Examiner   Date

DEDICATION

To the memory of my Beloved elder sister Sadiq O. Shefinat who would have been overwhelmed with joy to see me graduate as a chemical Engineer had death not over taken her so soon.

TABLE OF CONTENT

ABSTRACT

The purpose of this project is to identify factors (if there is any) that could possibly lower the performance of lead recovery plant as is obtained at West African Batteries Ltd and then suggest ways of improving on them.

In the course of the study, the lead recovery plant at West African Batteries LTD was visited for on the spot appraisal of the various processes involved in the recovery of lead from broken battery scraps. Consequently, datas were collected and analysed.

The analysis of the obtained datas show that the lead obtained is very much impure and hence the calculated efficiency is not the actual value. It also reveals that the percentage $PbSO_4$ (active ingredient) in the broken battery scrap is low and and hence the need to enrich it with other raw materials which are known to be lead rich such as antimonial dross. In order to improve on the quality and amount of lead out put. Other factors identified include, equipment maintenance and operational precautions and raw material preparations.

The analysis based on simplex method of linear programming shows that an optimum amount of pure lead output would require 48kg of iron swarf, 82kg of Na_2CO_3 and other reactants plus 570kg of scrap. The optimum performance/efficiency obtained is 68.3%. Also based on material and energy balances evaluated, a simple reverberatory furnace (batch reactor) is designed to produce 5000kg of pure lead per day.

CHAPTER ONE

1.0   INTRODUCTION

Among the nine known planets, the earth is a unique sphere that abounds with varieties of things -microscopic organisms, insects, plants, animals,and humans. In addition,the earth is a vast store house of wealth that contains every thing needed to sustain all that life.

The earth's chemical resources can be divided into several broad categories depending on our use of them; elments for metal production and technology: building materials; minerals for the chemical industry; and minerals for agriculture.

Metalic minerals can be classified according to their abundance. The abundant metals include iron, aluminium, chromium, manganese, titanium, and magnesium. While scarce metals include coper , zinc , tin, gold, silver, platinum, uranium, mercury, and molybdenum, and lead.

Availability of mineral resources is one measure of the wealth of a society. Those people who have been successful in the location, extraction or importation and use of minerals have grown and prospered. Without mineral resources, modern technological civilization as we know it would not be possible.

Today, many mineral products are found in many homes. Infact, the standard of living in a modern technological society depends to a certain extent on the per capita availability of mineral resources.

All other things being equal, ones standard of living increases with the availability in a useful form of all resources   including metals (Ferrous and Non - ferrous), non -metals, energy, soil, air and water. Our cleverness and skill allows us to overcome some problems of resource availability, but it is impossible to maintain an ever-growing population or a constant average standard of living because as the world's population and the desire for a higher standard of living increase, the demand for mineral resources expands at a faster and faster rate.From global point of view, our limited mineral resources and reserves threatens our affluence and the welfare of the future generations. Thus our resource problem is fundamentally a people problem i.e too many people chasing after a limited supply of resources.
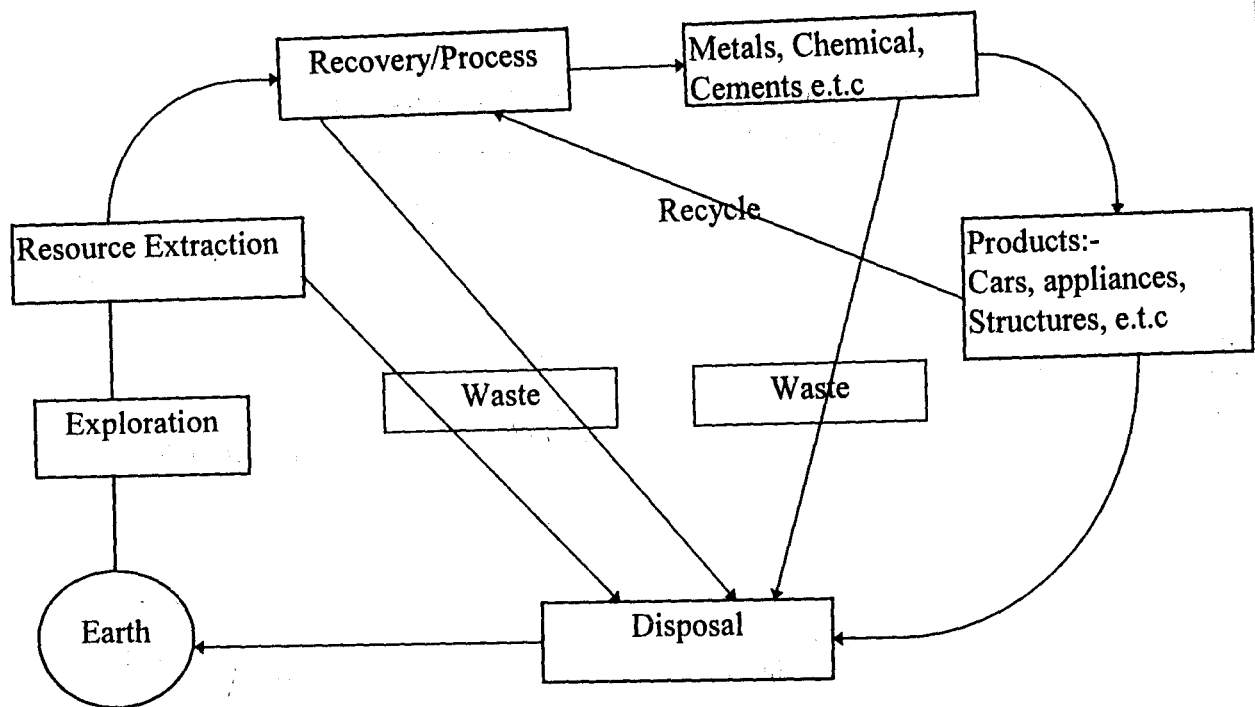
Fig. 1.0   Idealised flow of chart of the resource cycle

A careful look at the idealised mineral resource cycle shown above reveals that many components of the resource cycle are directly linked to waste disposal.

In fact, the major environmental impacts of mineral resource utilization are related to waste products. Wastes produce pollution that may be very harmful to humans, natural ecosystems and the biosphere.

They may attack and degrade other resources such as air water, soil and living things in other words, they may have an undesirable effect on the entire ecological systems.

So, useful consumption of mineral resources is that which minimize envirionmental degradation while at the same time allowing for continued use and conservation.One way of achieving this is effective recovery and recycling our mineral resources.

Primarily, the issue with mineral resource is not actual exhaustion or extinction, (because what is a resource and when it becomes limiting are ultimately social question that has to do with the level of civilization at that point in time) but cost of maintaining an adequate stock within an economy through mining and recovery/ recycling. At some time the input costs of mining a mineral outweights the output worth of the minerals.

If however, the availability of a particular mineral is threatened, there are only four (4) basic ways to deal with such a problem. They are as follows;

(i)   Find ore sources

(ii)   Find a suitable substitute

(iii)   Recovering and recycling of what has already been obtained as much as possible.

(iv)   When all of the above attempts fail, the only option left is to do without that material.

In reality, with the fixed amount of mineral resources, we are faced with the question of how we can use the available resources in the best way. A particular mineral can be used in several manners: rapid consumption, consumption with conservation or consumption and conservation with recycling.

The choice of any of these options however, may largely depend on economic, political and social factors. In this study, emphasy will be laid on one of such metallic (non-ferrous) mineral resources which is grouped among the scare metals - lead. And has thus found its use in the manner of consumption and conservation with recovery and recycling. Special concern will be placed on its recovery from used lead -acid accumulators (scrap batteries) in the manufacture of which lead has found special appeal over the years.

1.1   LEAD AND RECOVERY

Since used metal (scrap) is a major source of lead, the reclaiming of lead acid batteries which consumed nearly half of all the lead produced in the past has become very important. Besides, other factors which may neccessitate the recovery of lead after use include basically its relative indestructability after use and its pricing.

1.2   BENEFITS OF RECOVERY OF LEAD FROM SCRAP BATTERIES

As the word recovery implies it has to do with getting back what has been used in its original form. It is actually a secondary process of reclaiming a desired part of used product in its pure form. This process is beneficial for the following reasons;

(i)   The recovery of lead from scrap batteries is carried out in the market economies by private individuals who collect and process scraps and market the recovered metal.In short it encourages the establishment of secondary processing industries and employment .

(ii)   Social benefits - These benefits are the conservation of resources and the protection of the environment from the pollution of primary production and by reducing the amount of solid waste that would have been deposited on the ground as a result of the used products.

(iii) Production of lead from scrap batteries reduces the drain on ore deposits and also reduce the demand for mining.

(iv) Recovered lead which serve as secondary raw material is more concentrated and purer than primary raw material derived from ores. Scrap is already in the metallic state and

3

generally needs only refining and, in most favourable cases, only melting. The recovery of secondary lead therefore, can be carried out with fewer and simpler processing operations and usually less pollution than primary production.

(v)   Since recovery process usually requires less extensive processing than primary production, the use of scrap results in equipment savings and increases production capacity. Also, the capital costs of secondary processing equipment are appreciably lower than those of primary processing equipment.

(vi) The operating costs oflead recovery process is also generally lower although it could be labour intensive at times.

1.3   DISADVANTAGES OF RECOVERY OF LEAD FROM SCRAP BATTERIES

(i)   Lead is a very poisonous metal. It can do alot of harm to the human brain (when inhaled) and intestinal tract when consumed. Hence, the need to protect the personnels working on the recovery equipment is very great.

(ii)   The recovery of lead from scrap batteries can cause unacceptable levels of pollution, especially because secondary producers are generally located in densely populated areas. And also, the slag that results from the refining process is usually discarded which accumulates with time.

1.4   OBJECTIVE OF THE STUDY

Obviously , the recovery of lead from scrap batteries is prefered to primary minnig of lead ores from deposit in several ways. But for the recovery of lead from scrap batteries to be worthwhile, the concentrated metallic lead derived from such scraps must be very high and at a relatively lower cost of production. Based on this premise, this research is aimed at identifying factors which could contribute to a low yeild (if any), high average cost of production of an existing process and then make necessary recommendations on how the performance of the overall process can be improved.

1.5   METHODOLOGY

In the course of this study, the researcher went to West African Batteries Limited, Ibadan where he gained assess to their lead recovery plant for an on the spot appraisal of all the various stages involved in the lead recovery process. At the plant, he also held verbal interviews with the operating personnels including the "Smelter chemist" (who monitors the process), so as to get relevant informations from them.

4

1.6 SCOPE OF RESEARCH

This study is strictly confined to the lead recovery process as obtains at West African Batteries Limited, Ibadan. A company which has distinguished itself in the recovery of lead from scrap batteries and the recycling of such in the manufacture of high quality lead - acid accumulators for use in motor vehicles.

The recovery process as mentioned here, in this work is to be taken as a process that comes before a material is recycled. However, analysis is strictly based on the datas collected at West African Batteries Ltd.

These alloys have high fluidity and give sharp definition of printing characters. The fine detail from type metals has been erroneously ascribed to slight expansion during solidification. In reality these metals generally contract somewhere between 2-3 percent. Most type metals may be age hardend to improve wear resistance. Grain size in cast type metal depends upon cooling rate during solidification. Small alloy additions such as Lithium or magnesium may also be used to produce desirable fine grains.

2.2.3 Babbit: is a lead-base bearing alloy containing lead, tin antimony and usually arsenic. These are used for bearings in automotive engine connecting rod, dieselengine bearings, rail road car bearings, pumps, and construction equipment because it possess high antifriction properties.

2.2.4 Wood's metal: which melts at $67.8^{o}C$, has a nominal composition of 33.1%Pb, 14.3%Cd, 19%Sn, 33.6%Bi. This metal is used in fuse links for heat actuated water spray fire extinguishing systems.

Table 2.0   Composition and mechanical properties of lead alloys complied from "Metals Handbook" 1948 edition American Society for materials.

Alloy	Composition	Tensile strength (Psi)	Yield strength(Psi)	Elongation %	BHN	Typical Uses
Chemical lead	99.90 +Pb	2,385	1,180	29	-	Chemical storage tanks
Corroding lead	99.73+Pb	1,700	800	20	3.2-4.5	Storage batteries, cable sheating, paint calking, Antiknock fluid
Antimonial lead	99Pb-1Sb	6,100	4,800	60	14.5	Coatings, Body solder
Hard lead (aged)	94Pb-4Sb	11,670	-	6.3	24	Sheet, pipe
Soft solders	95Pb-5Sn	3,400	1,500	50	8	Coating and joining
	80Pb-20Sn	5,800	3,650	16	11.3	Coating and joing, Body solder
	50Pb-50Sn	6,100	4,800	60	14.5	General solder
Lead base Babbits (chill cast)	85Pb-10Sb-5Sn	10,000	-	5	19	Light loads, shafting
	75Pb-15Sb-10Sn	10,500	-	4	22	Moderate loads, pumps, Blowers
	83Pb-15Sb-1S+1As	10,350	-	2	20	High loads, Diesel engines
	83.5Pb-12.75Sb-3As-075Sn	9,800	-	1.5	22	Elevated temperature bearings, Trucks

2.3 USES OF LEAD AND ITS ALLOYS

As for applications lead probably has more varied fields of application than any metal. The greatest tonnage of lead used in the metallic form in either the commercially pure form or as lead alloy. A large quantity oflead is also used in chemical compound forms as white lead, red lead, lead chromate and tetraethyl lead which is used as an antiknock addition agent for petrol. Its formular is $Pb(C_2H_5)_4$.

Metallic lead is used for X-ray shielding (biological shielding), type metal, cable coverings, ammunition, bearing, calking, collapsible tubes, solder, tank-linings, coatings and as an alloy addition to steel, aluminium, bronze, and other metals to improve machinability.

Another field of application was opened for lead when plante'invented his lead storage batteries. Today, a good deal oflead goes to make plates for storage batteries (i.e lead-Acid accumulators employed in motor vehicles, aircraft, wind-power plants e.t.c

It is in the production of these lead storage batteries that a chemical compound-Litharge and some alloys of lead have found the widest use. And this serve the basic reason why used lead storage batteries are sources for lead recovery for recycle in the making of new lead storage batteries.

2.4 LEAD AND BATTERY (ACCUMULATORS)

An accumulator is an electro-chemical device for the conversion of electrical energy into chemical energy, the storing of that energy and the reconversion of that chemical energy when required into electrical energy. Over the years, lead has found a great appeal in the manufacture of such device. Alead derived accumulator is more consistently name the "lead-lead oxide cell" Its history can be traced back to 1859 with the construction by the French physist, Gaston Plate, of the first practical rechargeable Cell, consisting of two coiled lead strips, separated by a linen cloth. This system form the basis of the most widely used secondary battery (accumulators) of the present time. "Today over

11

a third of the world output of lead is used to manufacture over one hunderd million lead-acid battreries every year"

Like the dry cell, however, the lead acid battery is a direct current (DC) source using spongy lead, Pb, as negative electrode, its eletrolyte is dilute sulphuric acid, H_2SO_4 prepared by mixing with de- ionized water which eventually makes it up to a specific gravity of 1.265.
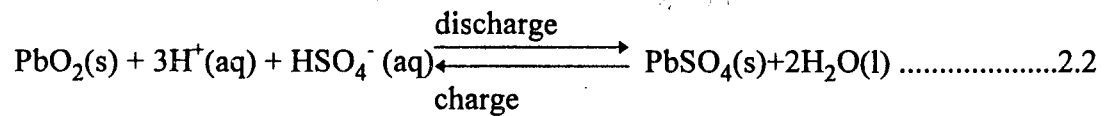
$$Pb(s)/PbSO_4(s)/H_2SO_4(aq)/PbSO_4((s)/PbO_2(s)$$
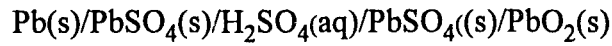
The overall electrochemical processes can be represented by the equation.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \underset{charge}{\overset{discharge}{\rightleftarrows}} 2PbSO_4(s) + H_2O(l)..................2.1$$
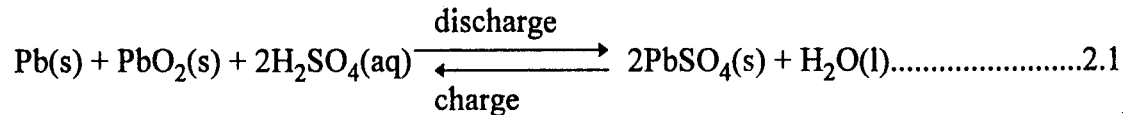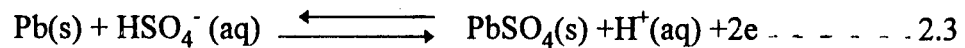
As the cell is discharged, Sulphuric acid is consumed and water is formed which eventually dilutes the acid further. The discharge process also result in the formation of insoluble lead sulphate on both electrodes. This meterial is a very poor electrical conductor and its deposition in a dense, fine grained form can shield and passivate the electrodes, so that the pratical capacity of a cell can become severely restricted. As discharge proceeds, the internal resistance of the cell rises, due to $PbSO_4$ formation and the decrease in electrolyte conductivity as H_2SO_4 is consumed. During Charge, however, $PbSO_4$ is reconverted to lead at the negative electrode and to PbO_2 at the positive eletrodes.

The electrochemical cells are usually expressed; Positive electrodes:

$$PbO_2(s) + 3H^+(aq) + HSO_4^-\ (aq) \underset{charge}{\overset{discharge}{\rightleftarrows}} PbSO_4(s)+2H_2O(l) ....2.2$$

Negative electrode

$$Pb(s) + HSO_4^-\ (aq) \rightleftarrows PbSO_4(s) +H^+(aq) +2e ------2.3$$

As shown above, it may just seem that the cycle of discharge and recharge can continue without an end. But certainly apart from the fact that this so called lead acid battery has a period of time it can live, there are other factors that could make it run out of use or obsolete. Shedding of active material from the plates and the accumulation of such

discharged material on the battery case floor can give rise to short circuits between positive and negative plates. This problem which can rather be prevented than corrected can cause permanent inactivity of the battery.

If a lead-acid battery is left for a prolonged period in an uncharged state or is operated at too high temperatures or with too high an acid concentration, the lead sulphate deposit is gradually tranformed by recrystallization into a dense, coarse-grained form. This process is known as Sulphatation and leads to sevice passivation, particularly of negative plates and therefore inhibits charge acceptance. Some damages such as terminal, connectors, containers breakage and linkage can render a battery useless. These sorts of battery are eventually collected and serve as source for lead recovery.

CHAPTER THREE

3.0   THE INDUSTRIAL LEAD RECOVERY PROCESS

3.1   EQUIPMENTS REQUIRED AND THEIR USES

The following are the various equipments used in the industrial recovery of lead from scraps batteries.

3.1.1   AXES

These are used for breaking open the containers of used or obsolete batteries so that the plates inside them can be collected.

3.1.2   BOATS

They are cylinderical containers made up of steel. Essentially, they are used to hold the feeds for weighing and loading into the furnace.

3.1.3   WEIGHING MACHINE

This is used for measuring the weigth of the feeds before they are finally emptied into the furnace. It is graduated in a way that can bear large weights.

3.1.4   FORKLIFT

This is a motor-driven lift that is used to carry large weights that ordinary man can not lift from the ground. It is used to lift the boat and its content for weighing and to empty the same content of the boat into the furnace.

3.1.5   REVERBERATORY FURNACE

This serves as the reactor for the thermal treatment of battery scraps and fluxes at high temperature. The heat energy is derived from burning of fuel. The solid materials melts under high temperature and are then subject to thermal and chemical treatment in the molten sate. Heat is trasferred to the battery scraps and fluxes via convention and hot wall.This furnace has intensity of mass and heat transfer due to the molten state of the material and also high process driving force as a result of high temperature.

This furnace which is made up of steel is specially lined inside with a refractory material called PYROCRETE. This helps to conserve the heat and also protect the body of the furnance against devastating effect of high temperature (Its thickness is between 5-7 inches). The rotation and the conical shape of the furnace which are design considerations enhance proper mixing and complete reactions. The reverberatory furnace is a typical batch reactor.

3.1.5 BAG HOUSE

In this recovery process (smelting) a considerable amount of fume is given off. The collection of this fume is important, both because of the damage it would do to surrounding vegetation and animal life and because considerable amount of lead would be lost. Bag house is used for collection of this fume. A bag house consist of rooms filled with long bags through which the smoke passes. The solid particles in the process smoke is retained by the bags , which are periodically shaken to remove the dust. The dust is treated to recover the lead in it.

3.1.7 MOULDS

These are thick walled steel containers which are used to collect the molten lead (when the recovery operation is completed) from the reveraberatory furnace. They are also used for collecting slag after the lead in the furnace has been exhausted.

3.2 RAW MATERIAL FOR THE LEAD RECOVERY PROCESS

3.2.1 The primary raw material required for the process is the broken battery scraps (i.e plates obtained from used batteries by breaking them up). This battery scrap contain basically lead sulphate ($PbSO_4$), an active ingredient that is readily converted to metallic lead in the reverberatory furnace. The broken battery scraps obtained from used batteries are often moist. Because of the presence of dillute electrolyte in the battery containers.

3.2.2 REDUCING FLUXES

These are the reducing agents that are usually reacted with the active ingredient in broken battery scraps in the furnace to effect the recovery of lead. They are usually fed into the furnace along side the broken battery scraps. These include

3.2.2.1 COAL

This is essentially carbon which is a good reducing agent.

3.2.2.2 SALTS

These includes anhydrous sodium carbonate (Na_2CO_3) and Sodium Chloride (NaCl) which make the slag fluidy for easy tapping.

3.2.2.3 IRON SWARF

Also a reducing agent which is used to eliminate surphur in form of FeS.

The above mentioned raw materials are often brought in by private individuals who act as suppliers to the company. And the company pays them money in return.

3.3   SMELTING OPERATION

Smelting is mainly a process of melting and seperation of the charge into two immiscible liquid layers at a high temperature and reducing conditions. Smelting provides a liquid slag-liquid metal seperation process which may be controlled so that a considerable amount of the impurities will seperate to and to be collected in the slag, leaving the liquid metal (matte) richer in the metal required to be extracted.

In this case, the desired metal is lead which is recovered from scrap battery components that make up the charge fed into the reverberatory furnace for smelting operation to be carried out on it.
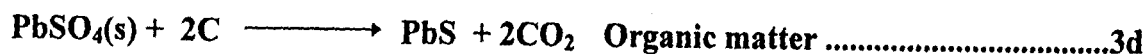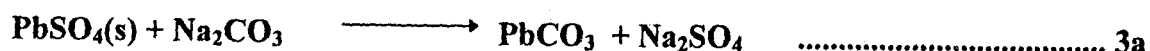
3.3.1   PROCEDURE FOR SMELTING

To start with all the battery scrap components and fluxes to be smelted are loaded into separate boats and then lifted with the use of fork lift onto the weighing machine (graduated in kilogrammes), one after the other. Their respective weights are then noted. By means of the fork lift, the boats are picked one after the other and emptied into the furnace.

The reverberatory furnace which is fired to a temperature of 1000^0C is then set in motion for upto one and half hours. The firing is done in such a way that the flame is directed over the top of the charge, so that the heating is indirect. The roof of the furnace is inclined which makes it tip sligthly towards the end of the furnace a way from the firing

16

end. This shape enhance proper mixing and reaction. Apart from that the combustion product of fuel are reflected or reverberated from inclined furnace roof ontothe charge.

At the end of one and half hour time period, lead is tapped out of the furnace into the iron moulds where it cools and solidifies. After the lead in the furnace has been exhausted, what comes out next and is also collected in the iron moulds is slag. This slag usually form on top of the liquid lead in the furnace helps to protect the lead from excessive oxidation and impurities in the charge and ash of the fuel are also prevented from conterminating the liquid lead.

3.3.2 FURNACE REACTIONS

$$PbSO_4(s) + Na_2CO_3 \longrightarrow PbCO_3 + Na_2SO_4 \quad \text{.......................................} 3a$$

$$PbCO_3 \xrightarrow{1000^0C} PbO + CO_2 \text{...}3b$$

$$2PbO + C \longrightarrow 2Pb + CO_2 \text{...}3c$$

$$PbSO_4(s) + 2C \longrightarrow PbS + 2CO_2 \quad \text{Organic matter} \text{.........................}3d$$

$$PbS + Fe \longrightarrow Pb + FeS \text{...}3e$$

3.3.3 RESULTS OF A MONITORED SMELTING OPERATION

The table below shows some data collected from the factory on a monitored smelting operation that was carried out for various batches.

Smelting Temperature : $1000^{\circ}C$

Reaction time : 1½ hour

TABLE 3.0 WEST AFRICAN BATTERIES LTD. LEAD RECOVERY RECORD (29-08-1998)

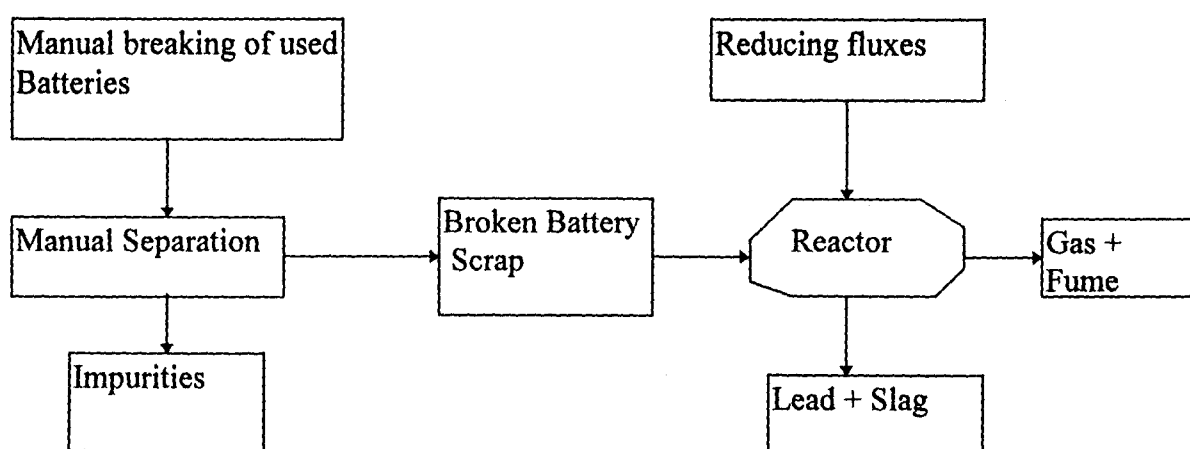| Shift	Batch Number	Input (Kg)	Output (Kg)		Fluxes (Kg)				Slag (Kg)
		Broken Battery Scrap	Metal Block	%Lead Recovery	Sodium Carbonate	Sodium Chloride	Coal	Iron Swarf	
A	1	700	669	95.57	70	15	60	75	120
A	2	705	450	63.83	70	15	60	75	205
B	3	610	406	66.56	70	15	60	75	270
B	4	800	855	106.88	75	15	60	75	283
B	5	700	374	53.43	75	15	60	75	326
C	6	705	590	83.69	70	15	60	75	230
C	7	619	565	91.28	70	15	60	75	110
C	8	500	483	96.60	80	15	60	75	116

KEY

A — Shift A (Morning)
B — Shift B (Afternoon)
C — Shift C (Night)

CHAPTER FOUR

4.0 EQUIPMENT DESIGN

This equipment design work is aimed at designing a recovery furnace batch reactor for the recovery of a specified amount of lead from scrap batteries per day. However, the design is not totally new but it is patterned around an existing one(i.e. one existing at West African Batteries Ltd). So, many of the parameters that will be used are obtained from the said existing one.

4.1 THE FLOW SHEET OF LEAD RECOVERY PROCESS FROM WASTE (SCRAP) BATTERIES

```
┌──────────────────────┐           ┌──────────────────┐
│Manual breaking of used│          │Reducing fluxes   │
│Batteries             │           └────────┬─────────┘
└───────────┬──────────┘                    │
            │                                │
┌───────────▼──────────┐  ┌──────────────┐  ▼           ┌──────────┐
│Manual Separation     │─▶│Broken Battery│─▶│ Reactor │─▶│Gas +     │
└───────────┬──────────┘  │Scrap         │  └────┬─────┘  │Fume      │
            │             └──────────────┘       │        └──────────┘
┌───────────▼──────────┐                         ▼
│Impurities            │                  ┌────────────┐
│                      │                  │Lead + Slag │
└──────────────────────┘                  └────────────┘
```

4.2 PROBLEM STATEMENT OF THE DESIGN

Lead is to be recovered from scrap batteries components in areverberatory furnace (batch reactor). A production rate of 5 tonnes/day of lead is required. The operating temperature is $1000^{\circ}C$ and at a total batch of 7500s i.e 5400s reaction time and 2100s shut down time for discharging and recharging. The stoichiometry of the reaction is same as shown in chapter 3 section 3.3.2

4.3   MATERIAL AND ENERGY BALANCE

4.3.1   MATERIAL BALANCE

The feed materials into the batch reactor are as follows; Scrap batteries ($PbSO_4$) dried.

Sodium carbonate, Na_2CO_3(100% pure)

Coal, C (54.8% pure)

Sodium chloride, NaCl

Iron Swarf (containing Fe^{2+}, 90% pure)

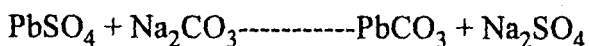Amoung the above mentioned feed materials are the limiting reactants viz:

Sodium carbonate, Na_2CO_3 = 70Kg

Coal, C 60Kg(Effective coal = (0.548 x 60 = 32.088Kg)

Iron swarf = 75Kg (Effective iron = 0.9 x 75 = 67.5Kg)

While the sodium chloride, NaCl (15Kg) is a tie substance.

From equation 3a i.e

$PbSO_4 + Na_2CO_3$-----------$PbCO_3 + Na_2SO_4$

Molar mass of Na_2CO_3 = 106

Mass of Na_2CO_3 = 70Kg

K mole of Na_2CO_3 = 70/106 = 0.660

Since the reaction is equimolar

Amount of required $PbSO_4$ = 0.660 x (207 + 32 + 64)

= 0.660 x 303 = 199.908Kg

Amount of formed $PbCO_3$ = 0.660 x (207 +12 +48)

= 0.660 x 267 = 176.22Kg

Amount of Na_2SO_4 formed = 0.660 x (23 x 2 + 32 + 64)

= 0.660 x 142 = 93.72Kg

According to the equation 3b, i.e

$$PbCO_3 \xrightarrow{\hspace{0.3cm}1000^oC\hspace{0.3cm}} PbO + CO_2$$
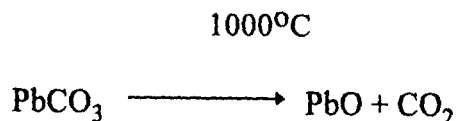
0.660 :   0.660 : 0.660

Amount of CO_2 formed = 0.660 (12 + 32)

0.660 x 44 = 29.04Kg

According to equation 3c i.e

$$2PbO + C \longrightarrow 2Pb + CO_2$$

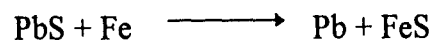$$===> PbO + \frac{1}{2} C \longrightarrow Pb + \frac{1}{2} CO_2 \text{ (Divide through by 2)}$$
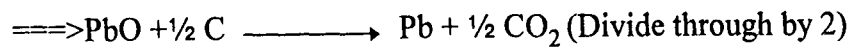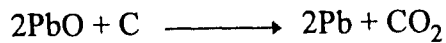
The amount of carbon (coal) used up = $\frac{1}{2}$ x 0.660 x 12 = 3.96Kg

The amount of lead, Pb formed = 0.660 x 207 = 136.62Kg

Amount of CO_2 librated = $\frac{1}{2}$ (0.660 x 44) = $\frac{1}{2}$ x 29.04 = 14.52Kg

According to equation 3e i.e

$$PbS + Fe \longrightarrow Pb + FeS$$

Effective mass of iron swarf = 67.5Kg
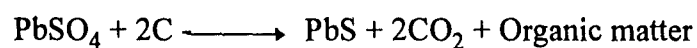
Molar mass of Fe = 56

Hence Kmol of Fe = 67.5/56 = 1.205

Since the reaction is equimolar

The amount of PbS required = 1.205 (207 +32) = 287.995Kg

Amount of Lead, Pb formed = 1.205 x 207 = 249.435Kg

Amount of FeS formed = 1.205(56 + 32) = 106.04Kg

From equation 3d i.e

$$PbSO_4 + 2C \longrightarrow PbS + 2CO_2 + \text{Organic matter}$$

1   : 2   :   1   : 2

The amount of C required = 2 x 1.205 x 12 = 28.92Kg

Amount of $PbSO_4$ required = 1.205 x 303 = 365.115Kg

Amount of CO_2 required = 2 x 1.205 x 44 = 106.04Kg

4.3.2 EQUATION OF MATERIAL BALANCE

Assuming no accumulation of material, the amount of material input must be equal to the material output. i.e

Material in = Material out...4.0

The material input as obtained from material balance are as follows;

Broken battery scrap (94.2% $PbSO_4$) dry mass = 600.00Kg

Sodium carbonate, Na_2CO_3 = 70Kg

Sodium chloride, NaCl = 15Kg

Coal C = 60Kg

Iron swarf = 75Kg

Total = 820Kg

Material output are as follows;

Lead output (sum) = 386.055Kg

Carbondioxide (sum) = 149.6Kg

Fume (ash) = 0.06Kg

Slag:

Sodium Sulhate, Na_2SO_4 = 93.72Kg

Iron Sulphide, FeS = 106.04Kg

NaCl = 15Kg

Organic matter = 130.905Kg

Total = 820Kg

Hence equation 4 is satisfied;

Table 4.0

COMPONENT NAME	INPUT (Kg)	OUTPUT (Kg)
Broken Battery Scrap	600 (94.2% $PbSO_4$)	-
Sodium carbonate	70	-
Sodium chloride	15	-
Coal	60	-
Iron swarf	75	-
Lead	-	386.055
Carbondioxide	-	149.6
Fume (ash)	-	0.06
Slag	-	284.285
Total	820	820

4.3.3   ENERGY BALANCE
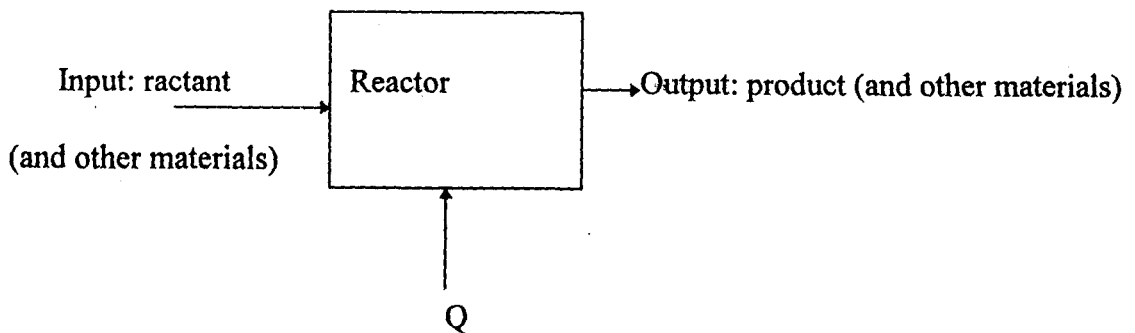
Input energy = Enthalphy of input materials + Q

$$= H(input) + Q ....(4.1)$$

Output energy = enthalphy of output materials

$$= H(output).....................................(4.2)$$

Equating equations (4.1) and (4.2)

H(input + Q = H(outpot)

therefore Q = H(output) - H(input)

where ΔH = H(output) - H(input)

$$Q = \Delta H..(4.3)$$

Input at 25°C = 298.15K

INPUT REACTANT AT 25°C	HEAT OF FORMATION ΔH_F AT Kg/Kgmol	AMOUNT (M) Kgmol	MΔH_F.(KJ)	MEAN HEAT CAPACITY Cp Kj/k Kg/Kg k	M.Cp Kj/k
$PbSO_4$	-914815.8	565.095	-516957834.5	137.3	77587.54
Na_2CO_3	-1128175.128	70	-78972258	121.0	8470.0
Coal : C	0	3288	-	1.30	42.744
Iron Swarf	0	67.5	-	0.50	33.75
			-595930093.5		86134.03

MCpΔT = 86134.038 (298.15 - 298.15) = 0

Hinput = -595930093.5 + 0 = -595930093.5Kj

Hinput = -595.9MJ

Output at 1000°C = 1273.15K

OUTPUT PRODUCT	HEAT OF FORMATION ΔH_F AT Kg/Kgmol	AMOUNT (M) Kgmol	MΔH_F.(KJ)	MEAN HEAT CAPACITY Cp Kj/k Kg/Kg k	M.Cp Kj/k
$PbCO_3$	-167.6	176.22	-29534.472	88.34	15567.27
Na_2SO_4	-330.50	93.72	-30974.46	137.3	12867.76
PbO	-51.72	147.18	-7612.1496	50.49	7431.12
CO_2	-94.052	149.6	-14070.1792	1.122	167.85
PbS	-22.38	287.995	-4645.3281	59,16	17037.78
Pb	0	386.055	0	28.47	10990.99
FeS	-22.64	106.04	-2400.7456	75.61	8017.62
			-91037.335		58069.39

MCpΔT = 58069.39 (1273.15 - 298.15)

= 58069.39 x 975

56617655.25 KJ   = 56.62MJ

Houtput = -91037.335 + 56617655.25

$\quad$ = 56526617.92Kj $\qquad$ = 56.53MJ

ΔH = Houtput - Hinput

$\quad$ 56.53 - (-595.9) $\qquad$ = 652.43MJ

From Equation 4.3

Q = ΔH = 652.43MJ

4.4 $\quad$ DETAIL DESIGN

4.4.1 $\quad$ SIZING OF REACTOR

4.4.1.1 $\qquad$ From the energy balance, the quantity of heat required is 652.43MJ

$\quad$ Fuel to be used for firing the reactor (furnace) is diesel which has a heating value of

39×10^6J/litre

$\quad$ Hence Volume of fuel required V_{fuel} = Q/39×10^6J/litre

$\quad$ = $\dfrac{652.43}{39}$ $\qquad$ = 16.73litres

4.4.1.2 $\qquad$ REACTOR VOLUME:

$\quad$ As obtained from simple material balance earlier 386.055Kg of lead is produced in $1m^3$ of reactor volume in total batch of 7500s. This is an average production rate of

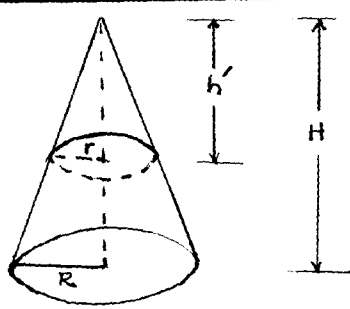386.055 x $\dfrac{24 \times 3600}{7500}$ Kgper day $\quad$ = 16.73litres

$4447.35Kg/daym^3$

i.e 4447.35Kg/day per m^3 of reactor volume. Since the required production rate is

5000Kg/day the required reactor volume is

$\dfrac{5000}{4447.35}$ $\dfrac{\text{Kgper day}}{\text{kg/day}} m^3$ = $1.12 m^3$

4.4.1.3 $\qquad$ DIAMETER AND LENGHT OF THE REACTOR:

The reactor is made up of a major cylindrical part that culminate at both ends in frustratrums.

$$R = 2r \text{---------}*$$

Based on dimensional detail of an existing one

$$\text{Radius} = 0.3 \times \text{Height} \text{------------------}4.4$$

$$h^1 = H/2\text{----------------------------------}4.5$$

Volume of frustrum = Volume of major cone - Volume of minor cone.

i.e Volume of frustrum = $1/3\pi R^2 H - 1/3\pi r^2 h^1$

$$1/3\pi(R^2 H - r^2 h^1)\text{--}4.6$$

Putting $h^1 = H/2$ in equation 4.6

$$\text{Volume of frustrum} = \frac{1}{3}\pi\left(R^2 H - r^2\frac{H}{2}\right)$$

$$= \frac{1}{3}\pi\left(\frac{2R^2 H - r^2 H}{2}\right) = \frac{1}{6}\pi\left(2R^2 H - r^2 H\right)$$

But r =R/2, therefore

$$\text{Volume of frustrum} = \frac{1}{6}\pi\left(2R^2 H - \left(\frac{R}{2}\right)^2 H\right)\text{----------------}4.7$$

$$= \frac{1}{24}\pi\left(8R^2 H - R^2 H\right)$$

$$= \frac{7}{24}\pi R^2 H \text{-----------}4.8$$

But R = 0.3H; ==> H = R/0.3 --4.9

putting 4.9 in 4.8;

Volume of frustrum = $7/7.2\pi R^3$

Hence total volume of frustrum = $7/7.2\pi R^3 \times 2$

$$= \frac{14}{7.2}\pi R^3$$

Hence total volume of the reactor = $\frac{14}{7.2}\pi R^3 + \pi R^2 h^{11}$------------------4.10

where h^{11} = height of cylinder= length of cylinder when it lies horizontally

$$h^{11} = R/0.3 \text{ ----------------------------------} 4.11$$

Putting equation 4.11 in 4.10

Total volume of reactor

$$\frac{14}{7.2}\pi R^3 + \frac{\pi R^3}{0.3} \text{ --------------} 4.12$$

$$= \pi R^3 \left(\frac{14}{7.2} + \frac{1}{0.3} \right) = \pi R^3 \left(\frac{14+24}{7.2} \right) = \pi R^3 \left(\frac{38}{7.2} \right)$$

$$= 5.28\pi R^3$$

Hence, $5.28\pi R^3 = 1.12m^3$ $==> 16.59R^3 = 1.12$

$R^3 = \dfrac{1.12}{16.59} = 0.068m^3$

$R = (0.068)^{1/3} = 0.41m$

Therefore inner diameter of reactor = 0.41 x 2 = 0.82m

Length of reactor = 0.82/0.6 = 1.4m

Diameter of the frustrum end = 1/2(0.82) = 0.41m

4.4.1.4   MIXING OF REACTOR CONTENT

The mixing of the reactants in the reactor volume will be accomplished by the rotary movement of the furnace-reactor. Since it will be pivoted on rollers that will be powered by an electric motor. Of course, what is most important is the optimum speed interms of number of revolutions per minute or seconds that will enhance proper mixing. That is to say that the speed must not be too high or too low to the extent that mixing would not occur. Hence, an electric motor that has variable speed will be appropriate (the design of this is more of Mechanical Engineering).
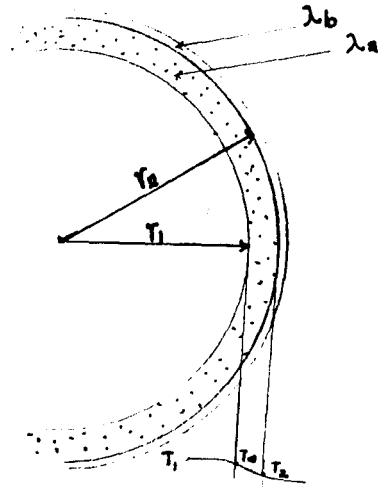
4.4.1.5   TAPPING HOLE

Since the process is batchwise, a convenient diameter for the tapping hole can be chosen so as to enhance the emptying of the products formed in the reactor. For this design, a diameter of 0.12m has been chosen.
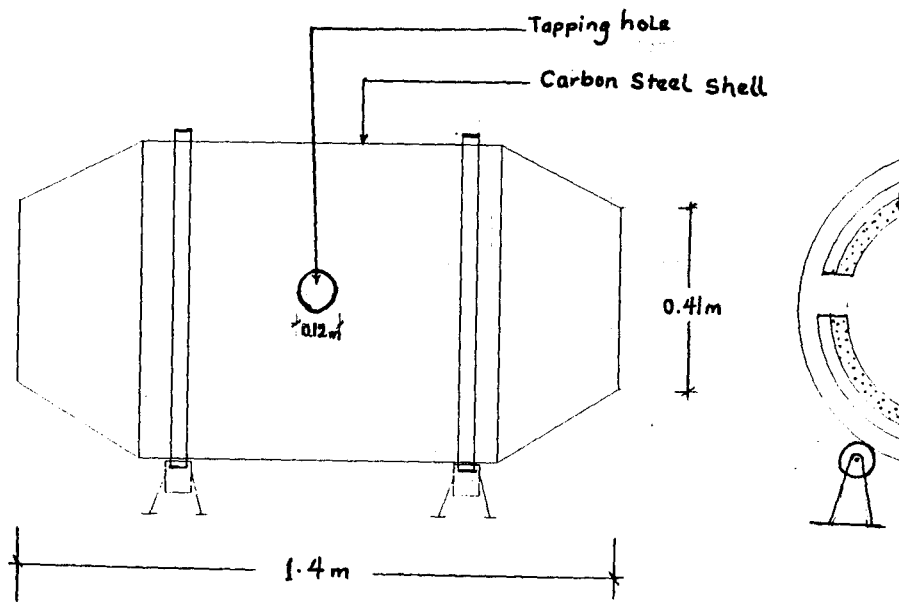
Fig.4.0   **Diagram of detail design**

$T_1 = 1000^\circ C$

$T_2 = 40\,^\circ C$

λ_a = thermal conductivity of fire clay = 1.745w/mk

λ_b = thermal conductivity of carbon steel = 16.269w/mk

r_1 = inner radius of reactor = 0.41m

r_2 = Outer radius of linning material (fire clay)

Heat conduction of a steady start flow heat through a composite multilayer cylindrical wall

is given as

$$Q = \frac{2\pi L(T_i - T_o)}{\sum \frac{1}{\lambda_i} \ln \frac{r_{i+1}}{r_i}} = \frac{2\pi L(T_1 - T_2)}{\frac{1}{\lambda_a} \ln \frac{r_2}{r_1} + \frac{1}{\lambda_b} \ln \frac{r_2}{r_1}}$$

$$Q = 8.7 \times 10^4 \, J/s \left(\text{i.e } \frac{652.43 \times 10^6 J}{7500s} \right)$$

$$r_2 = r_1 e^{\left[\frac{2\pi L(T_1 - T_2)}{Q\left(\frac{1}{\lambda_a} + \frac{1}{\lambda_b} \right)} \right]}$$

$$= 0.41 x e^{\frac{2 \times 3.142 \times 1.4(1000-40)}{8.7 \times 10^4 \left(\frac{1}{1.745} + \frac{1}{16.269} \right)}}$$

$0.41 \times 1.1155 = 0.4735m$

Hence the thickness of the linning material = $r_2 - r_1$

$r_2 - r_1 = 0.47 - 0.41 = 0.06m$

= 60mm

4.5 MATERIAL OF CONSTRUCTION

Many factors have to considered when choosing engineering materials for construction. These factors depend on mechanical properties of the material, functional requirements and constraint, design configuration, fabricability e.t.c. But for a furnace, the overriding consideration is usually corrosion and degradation resistance, Stability and cost.

Some metals have been known to loose their mechanical properties- tensile strength and value of Young modules at high temperatures. Hence at high temperature as it applies in this case of design, material that retain their strength should be selected. On this basis stainless steels are preferred to plain carbon steels.But in terms of cost, plain carbon steels are prefeered since it serve as an alternative.

So, for this design, plain carbon steel is selected as much as it will not be exposed directly to the high furnace temperature because it will be lined inside using fierd clay which is reltively cheap and is available when compared to other refractories such as zircon brick and pyrocrete which are expensive and scarce.

4.6 COSTING OF REACTOR (FURNACE)

The capacity of this reactor per year is 1825 tonnes (i.e 5 tonnes/day x 365 day/year). Hence it falls in the category of plant capacities under 60000 tonnes/year. therefore, step counting method of cost estimation for plants is applicable. It is given as

$$C = 112,300N(Q''/S)^{0.30} \text{ --------------------(4.6.1)}$$

where C = capital cost in pounds sterling (f)

N = Number of functional units

Q'' = Plant capacity, tonne per year

S = reactor conversion.

S = $\dfrac{\text{mass of desired product}}{\text{mass of reactor input}}$

$$= \dfrac{386.055}{600} = 0.64$$

Therefore, S = 0.64

N = 1

Q'' = 1825 tonnes/year

Hence, C =112,300 x 1(1825/0.64)$^{0.30}$

= £1221,531

If £1 = ₦150

Then, C = 1221,531 x 150

= ₦18.3 million

Note: equation (4.6.1) holds for only liquid and/or solid phase handling processes.

4.7   SAFETY AND LOSS PREVENTION

Lead is a very poisonous substance that causes malfunction of the brain cells when inhailed and digestive tract disorders when consumed with food. This shows that much care should be observed during production processes.Since lead vapourises at high temperatures in the ranges of thousands of degree celcius. So, operators working on the reactor should be provided with protective masks that would shield them from the lead vapours. The operators should also make sure their hands are thoroughly whashed before eating(eating around the plant should be discouraged).

Gases, most especially carbon dioxide that is given off during the process could cause much of environmental pollution if not checked.So to reduce the amount of this gas in the atmosphere,the gas stream should be scrubbed using organic solvent such as monoethylamine.

Certainly,if the above safety precautions are observed,loss of production,losses that could result from illnesses and death of operator(s) and much of environmental degradation would be reduced if not totally prevented.

CHAPTER FIVE

5.0   DISCUSSION OF RESULT

A closer look at the table of collected data shows that there is weight loss. That is to say that the output weight is not equal   to the input weight.This could be inform of:
Weight loss due to excessive evaporation of the moisture content of the charge. Because in most cases,the charge is usually wet. And as such the moisture contributes to the net weight of the broken battery scrap fed into the furnace.

Another reason for the weight loss could be due to drop outs from the furnace.It was observed that whenever the furnace was rotating, some parts of the reactor content leak out through the firing end.Of course, this causes a decrease in the net weight of charge that was measured into the furnace.

There could also be too much impurities in the charge. This is especially most likely since much of the scrap battery components are collected and supplied to the company by private individuals who would want to maximise profit at all cost. This motive alone could drive some of such suppliers into the temptation of adulterating their supplies (i.e mixing other things with their supplies). For the positive increase in the output weight of lead recovered in batch number 4, it could be attributed to increase in the input concentration of soda. It can be seen that the extra 5kg of soda added after about three consecutive batches caused a jump in the output lead recovered. It must have been that the accumulation from the previous batches was added to the liquid lead for this particular batch and was eventually tapped.

A closer look at the table shows that for any increase in the weight of soda after two or more batchwise operations had been carried out, there is usually an increase in the output lead recovered. This can also be seen in the case of batch number 8. These two cases are asssoicated with 'shifts' B and C.

However, based on this table, the average performance (bathwise0 evaluated stands at 82.23%. This ordinarily is high. But stoichiometric analysis shows that the lead obtained is very impure. So, the effective performance based on pure lead obtained will certainly be lower.

5.1   TREATMENT OF DATA COLLECTED USING LINEAR PROGRAMMING

To develop the constraints, the fraction of slag formed from Na_2CO_3 (x_1) and that formed from iron swarf (x_2) will be considered for a batch each from the three shifts studied.

For Batch 1 of shift A:

$$142 \times \frac{70}{106} x_1 + 88 \times \frac{75}{56} x_2 < 120$$

$$\Longrightarrow 94x_1 + 118x_2 < 120\text{------------constraint 1}$$

For Batch 4 shift B:

$$142 \times \frac{75}{106} x_1 + 88 \times \frac{75}{56} x_2 < 263$$

$$\Longrightarrow 100x_1 + 118x_2 < 283\text{------------constraint 2}$$

32b

For Batch 8, shift C:

$142 \times \dfrac{80}{106} x_1 + 88 \times \dfrac{75}{56} x_2 \leq 116$

$\Longrightarrow 108x_1 + 118x_2 \leq 116$ ------------constraint 3

To obtain the obective function that will be used to maximise the output of lead. The fraction of lead formed from Na_2CO_3 reaction (x_1) and that formed from iron swarf reaction (x_2) will be considered since lead recovered is a function of slag output i.e

$207 \times \dfrac{70}{212} x_1 + 207 \times \dfrac{75}{56} x_2 = Z$

$\Longrightarrow 68x_1 + 277x_2 = Z$

j \ i	68	277	0	0	0		
	x_1	x_2	x_3	x_4	x_5	B_i	
x_3 0	94	118	1	0	0	120	$\dfrac{120}{118}$
x_4 0	100	118	0	1	0	283	$\dfrac{120}{118}$
x_5 0	108	118	0	0	1	116	$\dfrac{120}{118}$
Z_j	0	0	0	0	0	0	
Δ_j	-68	-277	0	0	0	0	

Second iteration:

i \ j	68	277	0	0	0	
	x_1	x_2	x_3	x_4	x_5	B_i
x_3 0	-14	0	1	0	-1	4
x_4 0	-8	0	0	1	-1	167
x_2 277	108/118	1	0	0	1/118	116/118
Z_j	253.5	277	0	0	2.35	272.31
Δj	185.5	0	0	0	2.35	

From the reult of linear programming analysis of the data above, the optimal value

of the pure lead to be produced Z = 272.31Kg also, the fraction of iron swarf (x_2) of the

total amount to be charged is 116/118 with slack variable of x_3=4

x_4 = 167. Since x_1 (fraction of Na_2CO_3) to be charged as the exact amount of Na_2CO_3

would be used with respect to the stoichiometry of the reaction concerned.

It is assumed that higher percentage of the impurity comes from the organic matter

present, then slack variable x_4 = 167Kg correspond to the optimal value of organic matter

present and x_3 = 4Kg which is ash content.

From the stoichiometric analysis of the reactions, weight of Pb formed due to iron

swarf reaction with $PbSO_4$ is 249.435Kg

Total amount of Pb (pure) formed is 386.055Kg. Percentage lead (Pb) formed due

to iron swarf reaction to the total is

$\underline{249.435}$ x 100%

386.055   = 64.6%

So, for optimal value of pure lead to be produced which is 272.31Kg; it implies that

lead to be produced from iron swarf reaction is 64.6% of 272.31   = 175.95Kg

34

But 67.5Kg of iron swarf produced 249.435Kg of lead

$\underline{67.5}$ Kg of iron swarf will produce 1Kg of lead

249.435

Hence

$\underline{67.5}$ x 175.95Kg of iron swarf will produce 175.95Kg of lead

249.435

i.e 47.6Kg of iron swarf produces 175.95Kg of lead but fraction of iron swarf from linear

programming is 116/118

Hence actual amount to be charged = $\underline{118}$ x 47.6Kg

116

= 48.42Kg

From material balance

365.115Kg $PbSO_4$ forms 249.435Kg of lead from reaction involving iron swarf.

$\underline{365.115}$ x 175.95Kg of $PbSO_4$ will produce 175.95Kg of lead
249.435
from reaction involving iron swarf.

i.e 257.55 $PbSO_4$ will produce 175.95Kg of lead from iron swarf reaction.

From material balance, reaction due to Na_2CO3 requires 199,98Kg of $PbSO_4$,

while that of iron swarf requires 365.115Kg of $PbSO_4$.

Hence the optimum amount of $PbSO_4$ required in Na_2CO3 reaction

= $\underline{199.98}$ x 257.55Kg $PbSO_4$

365.115

= 141.06kg $PbSO_4$

From stoichiometry,

119.98Kg of $PbSO_4$ reacted with 70Kg Na_2CO_3

1Kg of $PbSO_4$ would react with $\dfrac{70\ Kg\ Na_2CO_3}{119.98}$

Hence for optimum value of $PbSO_4$ = 141.06Kg

$\dfrac{70}{119.98}$ x 141.06 Kg of Na_2CO_3 will be required

i.e 82Kg of Na_2CO_3

From above, the total pure $PbSO_4$ = 141.06 + 257.55 = 398.61Kg

Total organic impurities + ash = 167 + 4 = 171Kg

The Battery scrap to be fed (optimum) = 171 + 398.61 = 570Kg.

True efficiency in this case = $\dfrac{272.31}{398.61}$ x 100%

Optimum efficiency = 68.3%

5.2 CONCLUSION/SUGGESTIONS

As seen on the table of data collected it appears that the lead output or lead recovery is very high. But analysis shows clearly that the calculated efficiency is not the actual one. This is because, based on analysis, the lead recovered is more of lead alloy than pure lead. And more over the percentage $PbSO_4$ content of the scrap fed into the reactor is very low.

Certainly if the efficiency were to be calculated after the output lead had been subjected to treatments so as to obtain it in pure form, it would be discovered that the amount of pure lead is not that much.

However, to improve on this performance, the following suggestions would help:

Since lead recovered is a function of the percentage $PbSO_4$ present in the scrap fed, therefore, addition of lead-rich scrap to the broken battery scraps will improve the quality and output of lead. For example the broken battery scrap could be blended with antimonial dross which is known to be a rich source of lead.

Also, supplies who supply much of this broken battery scraps should be put into check. Because in an attempt to maximise profit they may adulterate their supplies with metallic impurities or organic matters that would add weight to their supplies and hence much money. Since they are payed according to the weight of scraps supplied.

Loss of reactor content can contribute to a low performance too. Hence, before the furnace is put into rotary motion, it should be fired for some minutes to enhance the melting of the top most layer of the reactants. So that when eventually the furnace is set on motion such materials will not be entrained in the air drift across the furnace hearth.

The scrap fed into the reactor should be thoroughly dried so that the true weight of feed materials can be ascertained. And apart from that, some amount of fuel that would be used to evaporate the moisture content would be saved.

Maintenance of equipment is also very important if such is to perform very well. For example it was observed that when the furnace at West African Batteries Ltd. was set in motion a considerable amount of reactor content leaked out of the reactor and were collected as drop-outs. Of course, this affects its performance.

For optimum amount of lead to be recovered, 82Kg of Na_2CO_3 and 48Kg of iron swarf should be used along with coal and 570Kg of broken battery scrap, as revealed by linear programming analysis.

5.3. APPENDIXES

5.3.1 MANIPULATION OF RESULTS/DATA COLLECTED

The calculation of efficiency reflected on the table of result in section 3.3.3 is obtained using the following relationship.

$$\text{Efficiency} = \frac{\text{Amount of lead recovered (kg)}}{\text{Amount of Broken battery scrap fed (Kg)}} \times 100\%$$

Hence for Batch;

1. efficiency = $\frac{669}{700}$ x 100%   = 95.57%

2. efficiency = $\frac{450}{705}$ x 100%   = 63.83%

3. efficiency = $\frac{406}{610}$ x 100%   = 66.56%

4. efficiency = $\frac{855}{800}$ x 100%   = 106.88%

5. efficiency = $\frac{374}{700}$ x 100%   = 53.43%

6. efficiency = $\frac{590}{705}$ x 100%   = 83.69%

7. efficiency = $\frac{565}{619}$ x 100%   = 91.28%

8. efficiency = $\frac{483}{500}$ x 100%   = 96.60%

Average efficiency/performance = $\frac{4388}{5339}$ x 100% = 82.23%

REFERENCES

1. H.S.Ray; A.Ghosh, "Principles of extractive metallurgy" 1991 (pp 136-138).

2. Kuzman Raznjevic, "Handbook of thermodynamic Tables and Charts" 1976 (pp 33,40-46).

3. Eugene A. Avallone and Theodore Baumeister III. "Marks'Standard Handbook for Mechanical Engineers", Nineth Edition 1987 (Page 4-64)

4. Coulson and Richardson, "Chemical Engineering" Volume 6, Second edition (pp 215, 245-248).

5. J.J. Moore, "Chemical Metallurgy," 1978 (pp 220-222)

6. Carl G. Johnson, William R. Weeks, "Metallurgy," Fifth Edition Revised by John G. Anderson P.E. 1976 (pp 347-358).

7. Colin A. Vincent; Franco Bonino, Mario Lazzari and Bruno Scrosati, "Modern Batteries. An Introduction to Electrochemical Power Sources". 1992 (pp 51-58; 95-108).

8. J.O. Odigure, "General Chemical Engineering Technology. Theory and Practical Application of Engineering Chemisrty", Fisrt Edition 1995 (Page 155).

9. Perry's "Chemical Engineering Handbook", 6th Edition Mcgraw Hill 1984.