RECOVERY OF LEAD FROM CONDEMNED STORAGE BATTERIES

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A thesis submitted to the Department of Metallurgical Engineering, BUET, Dacca in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Metallurgical)

DEPARTMENT OF METALLURGICAL ENGINEERING, BUET, DACCA.

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CONTENTS

CONTENTS (Continued)

CERTIFICATE

This is to certify that this work was done by me under the supervision of Mr.Mohammad Serajul Islam, Associate Professor, Department of Metallurgical Engineering, BUET, and it has not been submitted elsewhere for the award of any other degree or diploma.

Countersigned

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Signature of the Candidate

The undersigned recommend to the Department of Metallurgical Engineering the acceptance of the thesis "Recovery of Lead from Condemned Storage Batteries" submitted by Abu Syed Wais Kurny B.Sc. Engg.(Met) in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Metallurgical).

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ABSTRACT

The use of storage batteries for automobiles and other purposes are on the increase. But these batteries have a limited life. The aim of the thesis has been to see whether it is economically possible to recover lead from these condemned storage batteries. These batteries contain lead and a small amount of antimony.

The recovered antimonial lead may find its use in various industries like the type foundry, battery manufacture and even in ammunitions.

A small reducing type furnace was erected for the purpose. Experimental smelting of the battery plates containing lead-sulphate, lead oxide and some free lead was done.

Fluxing materials such as oxides of iron (Fe_3O_4, Fe_2O_3) and lime-stone was added to give a good slag.

Some considerations have been given to the possibility of recovering lead from the flue-dust.

An economy study has been made to see whether it is economic.

Chapter 1

INTRODUCTION

INTRODUCTION

Now a days, metals are the foundations of everything. Metals go to make among other things the frames of multi-storied buildings, the stream-lined bodies of jet planes, and the cigar-shaped hulls of space rockets. The demand for them grows as mankind climbs the ladder of progress.

In the 19th century, or a mere hundred and fifty years ago, less than one kilogram of metal was produced for every man on the Earth. The past hundred and fifty years have seen unprecedented advances in science technology, and industry. A dense network of power transmission, telegraph and telephone lines has been strung above.

The wooden plough has been replaced by gang ploughs hulled by tractors whose steel cylinders pack the power of a herd of horses. Wooden looms can now be seen mainly in museums.

All this progress has become possible because the per capita production of metals is now over 150 kgms and the total quantity of metals in machines, structures and buildings is about 4000 million tons. To date, technical progress is based on metals. Production of metals will keep growing as we become technically more developed.

In view of the rapid and expanding rate at which metal is being mined, it is natural to ask about our metal reserves - how much of the worlds ore reserve has been consumed and how much remains. This is a very interesting and crucial question but unfortunately

we have no definite and simple answer.

It is true we may have to use somewhat lower grade ores of iron, aluminium, and magnesium in future, but there need be no fear of ever exhausting the supply of the metals like iron, aluminium, magnesium etc.

For some of the commonly used but rarer elements such as lead, copper, zinc, the future outlook is not so promising, although it is very difficult to find out figures to establish definite conclusions.

There can be little doubt that with our modern production rates we are mining some ore deposits faster than new deposits are being discovered and, of course, this means eventual exhaustion. Owing to the limited resources of these metals attention has been given in all countries towards the recovery or the secondary extraction - which means recovery or extraction from scrap metals, drosses, sweepings, skimmings, wastes etc.

In our country
A large amount of iron, steel, aluminium etc. are discarded each year due to corrosion, as obsolete, and broken machine parts, worn out utensils etc.

Most of these scraps are remelted and fabricated into different useful articles and parts. Of the most abundantly available and useful metal scrap from which no attempt has yet been made to recover the metal, lead bearing scraps are important.

In our country, increasing quantities of scrap lead and lead alloys

are discarded each year, which can be worked up economically and conveniently for reuse.

These scrap lead appear in innumerable forms, but most of the tonnage will be covered by the following classifications[2]

1. Battery plates:

   Most motor cars are equipped with batteries in which the elements are made of antimonial lead. The expansion of the automobile industry causes the scrapping of increasing number of worked out batteries. The scrap contains antimonial lead, lead oxide, lead-sulphate wooden, rubber or plastic separators and some free acid.

2. Cable covering from discarded or burnt out cables.

3. Drosses from plants - which melt solder or white metal alloy in manufacturing or general use, such as foundries die casters, babbit metal users etc.

4. General lead-bearing scrap collected by junk dealers.

In order to determine whether a scrap is worth working it is necessary to know the nature of the scrap and how much of the contained metal may be expected to be recovered; it would be comforting to calculate the cost of production and to know the price of the metal in years to come. The availability and regularity of supply of scrap is a very important factor.

Of the many scraps of lead and lead-alloys, Lead-Acid batteries are most abundantly found in our country. One estimate says

that there are over 100,000 motor vehicles in Bangladesh. These vehicles discard over 50,000 condemned batteries each year. In the years to come, more vehicles are likely to be used and more and more batteries are sure to be discarded each year. The number of vehicles used by Bangladesh Army, which is of course a considerable figure, has not been included in this estimate.

In addition to these a large quantity of batteries are used in laboratories, hospitals, telephone exchanges railway engines and in loud speakers.

On the average each battery contains approximately 20 lbs. of lead and thus each year we waste more than 500 tons of lead.

However, these battery plates are worked for secondary metal in very small plants and by using very crude and primitive methods. Consequently the recovery is very small, in almost all cases only the free lead is recovered.

The aim of the present investigation has been to find out a possible means of producing lead, either hard or soft, from the condemned storage batteries. This has an important bearing on our home industry, where a primary production of lead is out of question.

As regards the recovery of lead from scrap battery plates, the problem, at the first glance, would appear to be simple because some of the lead is already present in the metallic form. But the recovery of more than 80 per cent of the metal content in very difficult.

The batteries as received may be in any one of the several stages of disintegration which makes sampling and therefore charge calculation difficult.

In spite of these difficulties it has been found that economical, rather profitable, recovery of lead from these scrap batteries is possible in our country.

1.

2

3.

Chapter 2

THE STORAGE-BATTERY

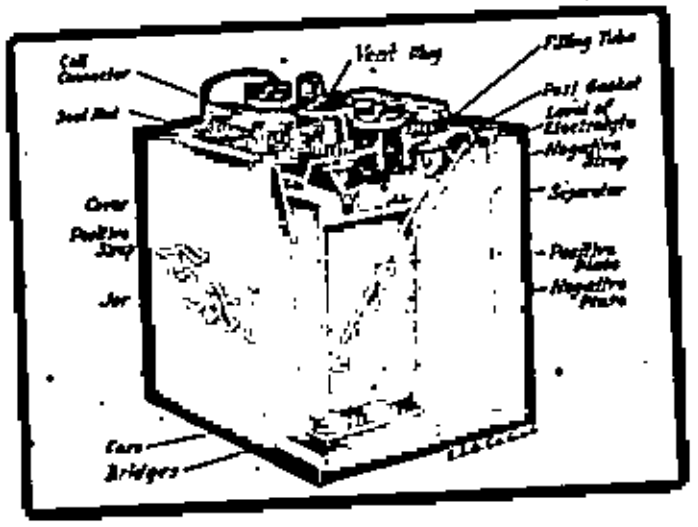
THE STORAGE BATTERY

The electric supply and storage batteries havebeen closely associated since the earliest days of direct-current power stations. Then very large storage batteries were an essential part of the power plant, providing electrical power which was switched on to the system either to supplement or to thke over generator leads during periods of heavy and light working.

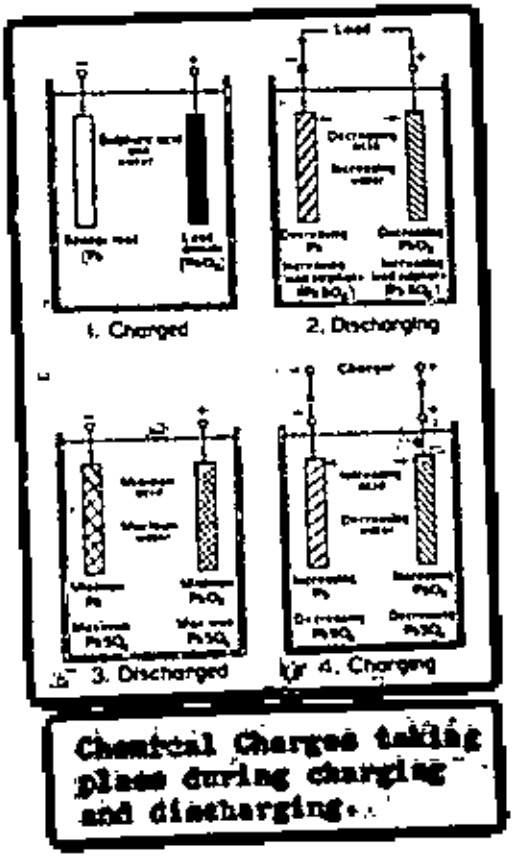
Changes from d.c. to a.c. generation and the development of national grid system have altered the demands made on storage batteries. Batteries or very large capacities are no longer required but because of the complexities of high voltage a.c. generation and distribution may more smaller batteries are used for a wide variety of duties.

Improved standards of living have created a large increase in the demands for telephones and all kinds of motor cars and road vehicles - none of these can work without a storage batteries. Other forms of transport, by air, rail and sea, rely on batteries for vital stand-by power. The replacement of steam locomotives by diesel and diesel-electric locomotives has increased the demands on the battery, which must new supply very high electrical power for starting large diesel engines, in addition to lighting loads.

Extensive building projects for new towns, schools, hospitals, large stores, place or entertainment etc. demand storage batteries for maintaing emergency services during power failures.



The Storage Battery



Chemical Changes taking place during charging and discharging.

Industrial efficiency is closely related to improved standards of material-handling relying largely on battery-electric powered trucks for transport and stacking duties.

The adaptability and reliability of storage batteries as sources of electrical power have made them an essential part of most industries throughout the world.

In all applications the battery has proved to be reliable and has frequently given good performance under adverse conditions and with indifferent maintenance. Much of the success of modern batteries lies in the research carried out since the war, resulting in improvement in battery components and production of design suited to various operating conditions. Battery life has been extended by the use of improved grid alloys, container and separator materials. Performance under widely different temperature conditions has been improved by new process methods and blending of oxides with new additives.

DEFINITION AND CHEMISTRY OF THE STORAGE BATTERIES:[4]

A storage battery is a chemical device reversible in action, which stores energy at one time for use at another. The energy stored is chemical and not electrical. Electrical energy in the form of d.c. electricity is applied to the battery during the operation termed charging. The electric current produces chemical changes in the battery and the chemical energy stored in the plates is reconverted to electrical energy when the cell is discharging.

Types of storage batteries which have most practical and commercial value are lead acid batteries and alkaline batteries, the latter including nickel-iron and nickel-cadmium assemblies. For our purpose we need to consider lead-acid batteries only.

LEAD-ACID STORAGE CELLS:

The fundamental parts of a lead-acid storage cell are two dissimilar plates or electrodes, immersed in an electrolyte in a suitable container, namely,

Positive active material - Lead peroxide, PbO_2

Negative active material - Spongy Pb

Electrolyte - Dilute solution of H_2SO_4 in water.

In a fully charged healthy cell the positive active material is dark chocolate colour and the negative active material slat grey colour.

CHEMICAL REACTIONS OF LEAD-ACID BATTERIES:

In general a storage battery must be given a charge before it can function and this is carried out by connecting a suitable low voltage d.c. supply across its terminals for a good number of hours. There are, however, some batteries which can be activated merely by adding acid. When a battery is fully charged the chemical changes taking place within the cell are complete. The positive active material has been converted to lead-dioxide(PbO_2) and the negative to spongy lead (Pb) in contact with the electrolyte of

dilute sulphuric acid.

CELL ON OPEN-CIRCUIT:

With no external circuit connected to the terminals of the cell, the two sets of ions within the electrolyte are in equilibrium and prevented from moving to the respective plates.

DISCHARGING:

During service when the battery gets discharged, a current flows in the external circuit from the positive to the negative terminal. Currnet also flows inside the battery between plates of opposite polarity by way of the conducting sulphuric acid solution.

It is in the dilute sulphuric acid (the electrolyte) that very important chemical changes take place when a current passes between the battery plates. This is very different from flow of of current (electrons) in the conductor across the terminals of the battery, which leaves the conductor completely unchanged.

Electrolytes are substances which in the liquid state or in solution, are largely dissociated into positive and negative ions or charged particles. Thus in solution a molecule of sulphuric acid (H_2SO_4) which is electrically neutral, is dissociated into one sulphate ion (SO_4^{--}) carrying two electronic charges and two hydrogen ions (H^+) each carrying a positive charge of an electron.

It is the migration of these ions to the electrodes (plates)

immersed in the sulphuric acid which causes electricity to flow within the cell. Most of the chemical changes take place at the surface of the plates in contact with the electrolyte, for it is here that the ions produce chemical changes within the active material.

CELL ON DISCHARGE:

When an external circuit is connected across the cell terminals the sulphate ions move to the negative plate and part with their negative charge. This produces an excess of negative charge on the plate, which is relieved by a flow of electrons into the conductor from the negative terminal to the positive terminal, i.e. from a point of low potential to one of higher potential. The passage of surplus electrons from the negative plate to the conductor allows more sulphate ions from the electrolyte to combine with the lead to form lead sulphate ($PbSO_4$).

At the positive plate, the highly oxidised lead dioxide (PbO_2) is short of negative charge, so that it readily accepts the electrons arriving from the conductor. Hydrogen ions now move into the positive plate from the electrolyte and combine with oxygen to form water. This leaves some lead free to combine with the sulphuric acid to form lead sulphate and more water.

As the discharge proceeds and current continues to flow, more lead sulphate is formed, in both plates, by combination of the acid from the electrolyte. Water also is formed which helps to dilute the electrolyte and it is this progressive weakening of

the electrolyte by the formation of water which provides a convenient way of measuring the amount of discharge taking place. The cell is discharged when its voltage falls rapidly and at this stage most of the active material has been converted to lead sulphate and the plates are almost identical in chemical composition.

CELL ON CHARGE:

To reverse the chemical changes taking place in the cell during discharge, it is necessary to pass a current into the cell in the opposite direction to that of discharge.

The charging source must therefore have a voltage greater than that of the cell or battery to be charged. The charging source connected across the cell supplies an excess of negatively charged electrons to the negative plate and creates a shortage at the positive plate. The result is that hydrogen ions (positively charged) are attracted to the negative plate, where the hydrogen combines with the lead sulphate to form lead (Pb) and acid (H_2SO_4).

The shortage of charge produced at the positive plate results in the sulphate ions being attracted and combining with hydrogen of the water to form sulphuric acid.

Some of the oxygen of the water combines with the lead of the positive plate to form lead oxide. At the negative plate the process of recombination of the hydrogen and sulphate continues as long as there is sulphate present. When the process of conversion of lead sulphate to lead is almost complete, hydrogen bubbles

form at the negative plate and rise through the electrolyte.

Similarly sulphate ions react with water at the positive plate f forming sulphuric acid and leaving oxygen to react with lead to form lead oxide. When most of the lead is converted, the oxygen appears as gas at the positive plate. The formation of hydrogen and oxygen gas at the plates is a sign that the cell is reaching the fully charged condition.

As the charge proceeds acid which is released from the plates passes into the electrolyte and the specific gravity slowly increases.

The chemical reaction can be expressed as follows :

$$\underset{\text{Discharged}}{PbSO_4 + PbSO_4 + 2H_2O} \rightleftharpoons \underset{\text{Charged}}{\underset{(+ve)}{PbO_2} + \underset{(-ve)}{Pb} + 2H_2SO_4}$$

The arrows are used instead of an equals sign to indicate that the reaction is reversible.

It will be appreciated that the normal working of a battery produces lead sulphate at both negative and positive plates, which are reconverted to their original condition by charging.

<u>WHY BECOME CONDEMNED:</u>

The formation of lead sulphate ($PbSO_4$) during the normal discharge of a cell reduces the porosity of the plate, because the sulphate occupies more space than the original active material.

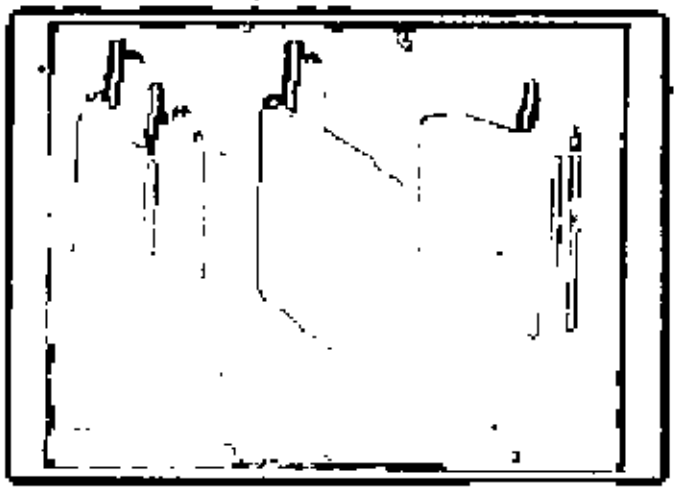
Normally the expansion is taken up by the pores of the plates being compressed and no harm results. It, however, the sulphate formation is excessive owing to the cell being persistently over discharged and under charged or left for long periods in a discharged condition, the sulphates expands beyond the absorbing capacity of the pores.

If the sulphates formed during discharge is allowed to exist for an appreciable period of time the crystals seem to become rearranged and form a more dense mass which is more or less difficult to convert to healthy material by normal charging.

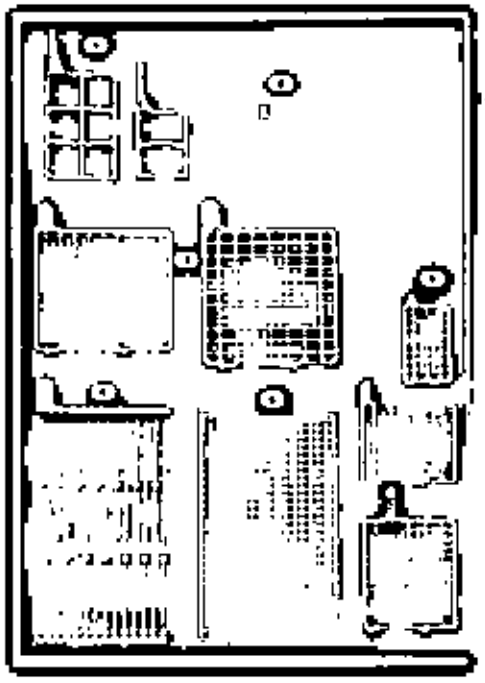
The presence of this unhealthy sulphate is indicated generally by loss in capacity, low voltage on discharge and abnormally low specific gravity of the electrolyte. It is also some times aparent to the eye through the presence of spots on the plates or by the change of colour on the positive plate form definite dark brown to a lighter brown or by the slate grey of the negative to a lustreless whitish grey.

For many years antimony has been the alloying element added to lead in making the lead-acid battery grids. Alloys containing 6 to 9 per cent antimony are excellent from the production point of view. However, they suffer from intergranular oxidation[1] during service which is accelarated by the presence of eutectics at the grain boundaries. Antimony also is released into the electrolyte and during charging is deposited together with spongy lead on the negative plate.

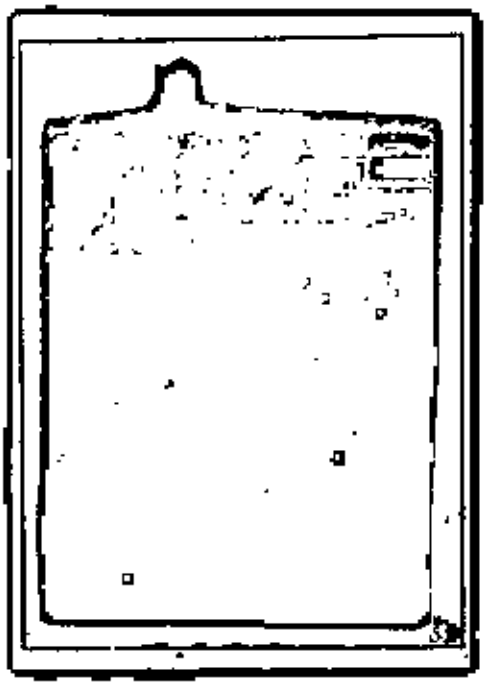
This is is also to some extent, responsible for the batteries being condemned.



Battery-plates as they are arranged in a cell.



Various types of grids



A negative-plate, when condemned and exposed to the atmosphere.

ANALYSIS OF THE PLATES AND GRIDS:

An actual analysis carried out in the laboratory revealed the following composition :

Positive Plate	Pb. content
$PbSO_4$ = 45.6%	31%
PbO_2 = 44.4%	30%
Residues, moistures = 10%	

Negative plate	
$PbSO_4$ = 53.2%	36.28%
Pb = 36.6%	36.8%
Residues, Moistures = 10%	

Lead-Antimony Grid

Lead = 90%

Antimony = 7.2%

Moisture, Residues = 2.8%

PROPORTION OF BLACK POWDER, RED POWDER AND GRID:

Black powder : 35 pct.

Red powder : 43 pct.

Grid : 22 pct.

Therefore the metal content per hundred pounds of scrap battery plates is 76 pounds.

The charges could not be thoroughly dried and so small amounts

of moisture and H_2SO_4 was present with the plates. We have assumed this figure to be 10 pct. of the total weight of scrap battery plate. This reduced the lead content per hundred pounds of charge to 68 lbs. On this basis the results were calculated.

Chapter 3

CHOICE OF THE METHOD

WHY BLAST-FURNACE

The choice of the vessel in which to carry out the reactions which lead to the production of lead is governed firstly by the natur of the concentrates and of the fuel available. The second factor to be considered is the technological knowhow and cost of production. It is, however, difficult to come to an absolute decision.

Regarding the recovery of lead from battery plates four different methods[5] of treatment have been suggested each of which has good points and some draw-backs. An attempt has been made in the following sections to compare the different methods available and to come to a conclusion regarding the method to be used.

SMELTING IN THE ORE HEARTH:

This, the oldest method of treating lead ores, has been many ups and downs. Originally it was the only method of treating high grade ores, but the introduction of the blast furnace with its high capacity and ability to treat impure ores caused much of the ore-hearths to shut down.

This method of smelting was based upon (1) the reduction of lead oxide by C or CO and (2) the reaction between lead oxide, lead sulphide and lead sulphate, resulting in a double decomposition and the formation of lead and sulphur di-oxide.

The process carried on is mainly the old 'roast reaction' in which the lead sulphide at relatively low temperature is oxidised to

a mixture of oxide and sulphate. The temperature of the mass is then raised, the oxide and sulphates are reduced by excess of lead sulphide to lead and sulphur dioxide.

The recovery of lead may, in exceptional instances, be as high as 85 per cent but normally ranges from 65 to 75 per cent with a coke requirement of 3 to 5 per cent of breese.

In ore-hearth a good deal of lead are volatalised and the grey slag produced contains a considerable amount of lead and consequently must be treated in a blast furnance.

Although it has some advantages like ease of nonstruction and operation this method is not suitable for our purpose for the following reasons :

1. The recovery is less.
2. There is a high fume production and the fume must be recovered if operations are to be profitable.
3. The slag needs subsequent treatment in a blast-furnace, thus increasing the cost of production.
4. The tonnage that can be treated is small.
5. Working on an ore-hearth is laborious and unhealthful.

LEACHING AND SMELTING:

This method has been proposed by Prof. Carle Hayward of M.I.T., which gives promise of solving many of the difficulties of lead battery smelting.

The scrap is first leached with a cold concentrated solution of

sodium carbonate, removing particularly all the sulphur. The smelting procedure was also altered with the object of (a) reducing the temperature so that the operation could be carried on in steel containers, (b) using a flux which will absorb antimony with little or no lead, (c) reducing antimony in the slag with carbon to a metal and at the same time regenerating the slag for reuse as flux, and (d) making the process continuous.

In spite of all these advantages it has some difficulties :

(1) The installation and operation of the furnace on a counter-current principle will be much more expensive if not impossible in our country.

(2) The desulphurisation of the charge by leaching before smelting introduces further complications in the process.

(3) Time and cost of production will be greater.

(4) Difficulties in operation and availability of the flux, especially fluorospar is to encountered.

REVERBERATORY FURNACES:

Some operators use a stationery reverberatory furnace for treating the battery plates or the by-products, but it is found that this type of furnace can handle only about 20 pct. of the tonnage of a blast-furnace. The tilting reverberatory tends to make the operation somewhat more flexible and the tonnage treated slightly higher than with the stationery type, but it too has a capacity much less than the blast furnaces.

In reverberatory furnaces 2 procedures are possible. One is to

reducing agent, such as coal, and produce an antimonial lead as in blast furnace. The other is to fuse under oxidising conditions to produce a slag consisting mainly of lead-antimonate and leaving the metal in the form of soft lead. This metal is kettle refined and cast into ingots. The slag is smelted in a blast-furnace or reverberatory furnace under reducing conditions to produce antimonial lead. This furnace has the following difficulties:

1. Cost of construction is high.
2. The labour cost in reverberatory lead smelting would also be higher than blast-furnace operations and recovery is less.
3. Control device is costly.
4. Less tonnage treated.

BLAST FURNACE:

The entire battery may be smelted in a blast-furnace, as we would smelt an ore, thus recovering the lead and antimony as an alloy. While simple and direct, this method has 3 disadvantages:

1. A rather high temperature is required to liquify properly slag matte mixture resulting from the smelting of such impure materials, which in turn cause high losses in fumes.
2. The sulphur in the charge produces considerable matte which not only is so low grade as to make sale difficult but also results in serious losses in lead and antimony.
3. The antimonial lead so produced cannot be used directly for the making of new plates without adding more antimony.

from such smelting will be lead, slag and flue-dust. In the industry lead produced from battery are called soft lead even though it contains 2 to 5 pct. antimony. If it contains more than 7 pct. antimony if is called hard lead.

In spite of the difficulties mentioned above we may modify our c charge make up and operate the plant with advantage as well as p profit. The following are the advantages of using a blast furnace:

1. It has the ease of construction.
2. Cost of construction is lesser and installation easier.
3. Only this process favours the disintegration, though at a high temperature, of the sulphates forming a major part of the charge.
4. Permits the interaction between the PbS and PbO, by virtue of the prevailing circumstances.
5. Extreme care is not needed in its operation.

In smelting any type of ore by any method, the sulphur must be largely removed and the impurities must be combined in a slag, fusible at as low a temperature as possible and of considerably low specific gravity. In order to ensure satisfactory separation from the liquid metal it should be very fluid.

None of the processes, excepting the blast-furnaces, give a finished slag or waste product at one operation that can be discarded and final treatment of their product is usually completed in the blast furnace. For all these reasons, by far the world's major part of lead - either primary or secondary is produced by smelting in a blas furnace.

Chapter 4

BLAST-FURNACE

The furnace used.

BLAST FURNACE

All parts of the furnace need very careful determination, with due respect to the type of raw material used. An illproportioned furnace will never give smooth working. The lines of the furnace must be so designed as to allow the smooth descend of the stock, during which time the materials are progressively heated, reduced and finally melted.

As the burden descends the shaft of the furnace, carbon deposition may cause hanging. This tendency to hang is overcome by outward batter. Lower down the shaft or stack, at temperatures where carbon deposition is less prone to occur, the burden becomes sticky causing wall drag, which necessitates outward batter. By the time that the raw materials have reached the bosh, reduction should be complete or nearly complete and the burden gradually becomes fluid metal and slag. This results in a contraction in volume and the regular descend of the burden in the bosh demands inward batter towards the tuyeres.

Unless inward batter is provided to compensate for the volume reduction, the sinkage of the charge from stack to the hearth will be irregular. If the inward batter is too great, resistance to the downward flow of the charge will lead to irregular operation. If too small, the materials are likely to drop in an irregular manner.

This change from outward to inward batter frequently requires

a parallel portion, the cylinder or barrel, so that the correct angles may be established. The walls of the crucible are parallel, no volume change taking place, but the dimensions of the crucible are of considerable importance.

The furnace employed for the purpose is a miniature blast-furnace with a very simple arrangement for flue-dust recovery. A drop-bottom arrangement similar to that in cupola to facilitate intermittent working and subsequent cleaning and repairing of the furnace has been used. A small door is provided at the lower part to prepare the bottom of the furnace. No cooling of the refractories is done, except that the outer surface of the metallic shell is exposed to the atmosphere. The charging is similar as in the case of a cupola consisting of alternate layers of coke and metallic charge - with an initial layer of coke which is the bed-coke.

A wind-belt, as is used in a cupola, has been provided to evenly distribute the air among all the four tuyeres. The cold blast is provided by a motor driven blower, which is connected to the wind belt by a steel pipe.

The shell is made up of a 1/16" steel-sheet. The vertical seams in each section are welded, but the entire height is covered by 5 segments, each resting upon another. For ease of repair or replacing the brick lining the entire shell is divided in two parts, which are bolted together. The entire furnace rests upon a steel-ring supported by four steel-pipe pillars. The pillars are held to the ground by concrete foundation. In view of the fact that the total weight of the furnace together with

charge have to be supported by the foundation and any appreciable sinking of the base would result in serious troubles, this part of the furnace should be made specially strong.

A very small platform is provided for smooth charging through the top of the furnace.

The furnace, when operated smoothly have the following well defined zones[6] :

CRUCIBLE OR HEARTH:

It is the region where the molten metal is accumulated prior to tapping and extends from the bottom to the tuyeres. The depth of the hearth, will depend on the time interval at which the metal is desired to be tapped. There should be a slag hole just below the tuyeres and is kept open during the operation. The tapping time is indicated by the run out of the slag. A slag hole was provided, but because of the low quality of fire-bricks the hearth capacity could not be fully exploited. This led to the eventual closure of the slag hole by a piece of fire-brick. Moreover the slag was not fluid enough to cause effective separation and to come out through the slag hole.

On the hearth of the furnace the only solid that should be present is coke; this will be in small pieces after traversing the combustion zone. The liquids are antimonial lead, and slag.

TUYERE OR COMBUSTION ZONE:

As the name signifies it is the regions where the tuyeres are placed and the combustion of coke to CO_2 takes place. This CO_2 is immediately converted to CO by the excess of red-hot coke, so that immediately above the tuyeres we are left with CO and N_2. The combusion zone is the region in which lead is volatalised in greatest quantity. A little will be condensed in the charge above this zone, but the intention is that the stock column should be easily penetrated by gas. The bulk what is volatalised will escape as fume.

MELTING ZONE:

Above the combustion zone, the solids are coke and unreduced oxides and sulphates. In this zone, hot gases are rising to heat the charge, and relatively cold metal is running down through the charge, so cooling the hot gases, this cooling compresses the zone. The lower the melting point of the metal and the more easily it is reduced, the greater is this effect.

From the point, the charge materials start to soften, the coke has to bear the whole weight of the charge down to the hearth. This zone is practically also the reducing zone, and is termed as the melting zone, due to the fact that immediately after the reduction is complete, fusion of the metal takes place and it falls down as drops of molten metal at the bottom of the furnace.

STACK OR CHIMNEY:

This is no separate structure in the sense that it is only the projection or elongation of the main shell constituting the

combustion and the melting zones. The function of this zone is to stock the metal charge, coke etc.

The hot ascending gas heats and dries the fresh solids. Depending on the gas velocity and cleanness of the material packing a certain amount of fine material is driven over with the fume into the gas offtake.

In this description of what goes on inside the furnace, it is imagined that gas can pass freely through the charge, and can reach all parts of each zone; this ideal state of affairs can be broken down at once by the introduction of fine material into the charge. Careful charge preparation, therefore, is of vital importance to the successful running of a blast-furnace; that is not to say that money cannot be made by feeding any junk into the furnace, but that more money can usu be made by first getting that junk into a suitable physical shape.

DRYING OF THE FURNACE:

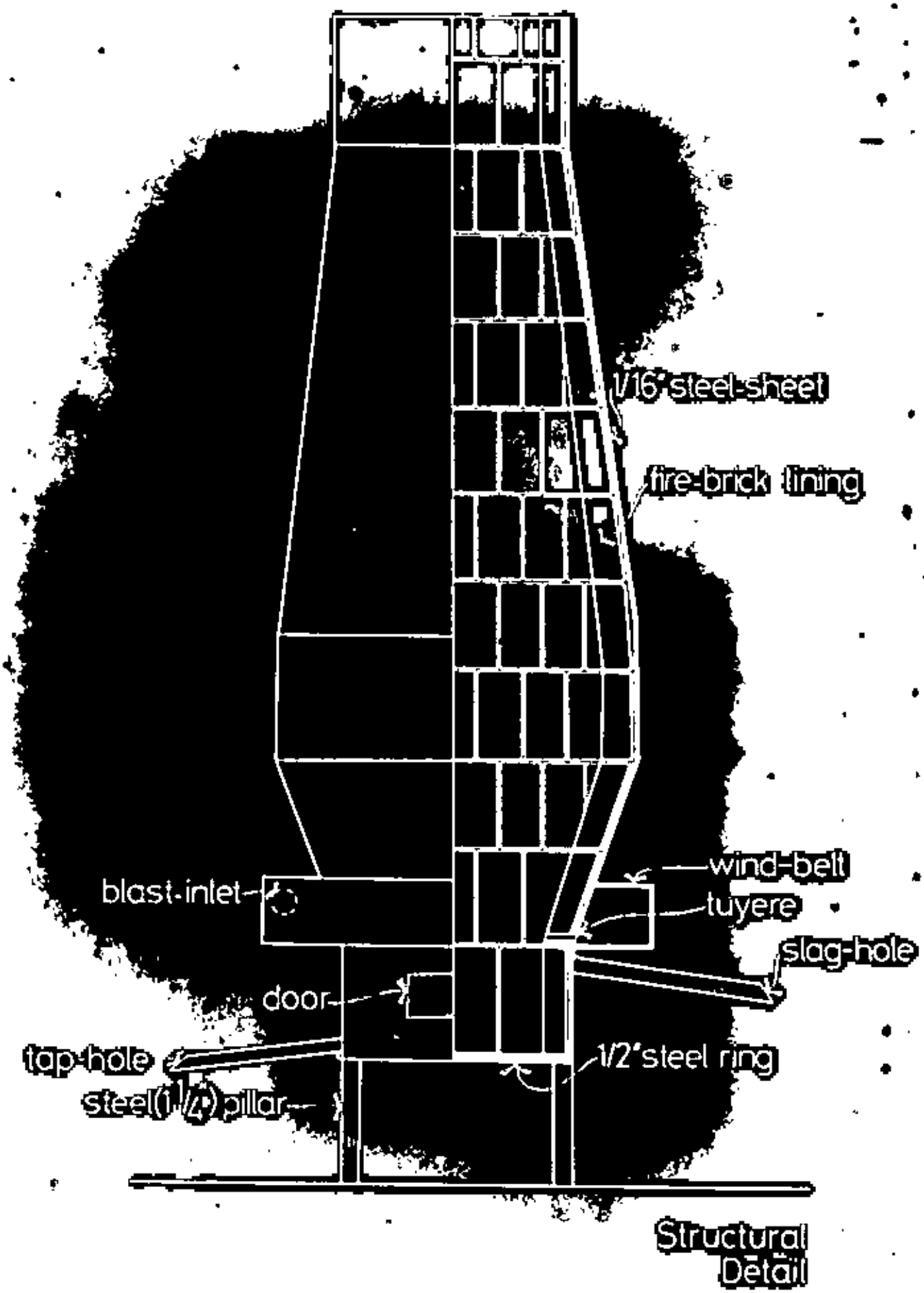
There is no standard practice of blowing in a blast-furnace. The d methods adopted largely depends on local conditions and custom. The preliminary drying of the lining is most important. The careful and thorough drying of the lining, preferably course by course, cannot be over-emphasised. Some times this is done by wood and coke fires in the hearth, sometimes by hot blast and blast-furnace gas. Any time and trouble taken in assuring careful and gradual drying of the furnace is more than repaid in its subsequent operations.

This is done in the following way, when the furnace had been air-dried,

a scaffold of timber was built just above the tuyere level. The space below this level was filled with kindling wood and shavings saturated with oil. These were admitted to the furnace through the bottom door, — which was left open for the purpose.

The furnace was then lit. After sometime a light blast was turned on. When they were burned to ashes, the blower was turned off. Again, on another occasion, the furnace was lit as before, and coke was then charged to raise the temperature somewhat higher than before. To determine the temperature, a cast-iron piece was used. As it melted, it could be concluded that the temperature was higher than 1200°C, which is enough for the purpose. After each heating the blast-furnace lining is carefully examined to see whether any cracking has taken place due to improper fusion of the fire-cement. After the heating by wood fire no cracks were found to develop and so patching was not necessary. After the heating by coke it was found that some cracking has taken place, especially in the combustion zone. The cracks were carefully patched up by fire-clay cement and some time was allowed for natural air drying.

Thus the drying became complete and the furnace was ready for actual smelting operation.



Structural Detail

Chapter 5

CHARGE MAKE-UP

CHARGE MAKE-UP

Before beginning with the actual smelting, we must find out the proper proportions of each constituents which should be charged. A knowledge of the separate constituents, regarding their physical and chemical aspects is therefore essential.

The input in a blast furnace for the smelting of battery plate should consist of -

1. Lead bearing materials.
2. Coke, acting both as fuel to supply the heat for smelting and as the reducing agent (either as solid carbon or gaseous carbon monoxide)
3. A suitable flux or a combination of fluxing agents for removing the gangue material.
4. Air for combustion reactions.

LEAD BEARING MATERIALS:

Before going to calculate the charge make-up we must carefully find out the lead containing materials in the lead acid batteries. The battery consists of the following parts: containers, cell connectors, positive and negative plates, separators and of course the electrolyte.

CONTAINERS:

Containing jars may be open and closed and are made of the following materials: glass, hard-rubber compositions, celluloid and gumsite.

The most extensively used jars in lead-acid battery practice are hard-rubber type. Celluloid jars are moulded or built up. Plastic celluloid, a mixture made up by treating nitrated cellulose and gum camphor in ether may be pressed to jar form in a mold.

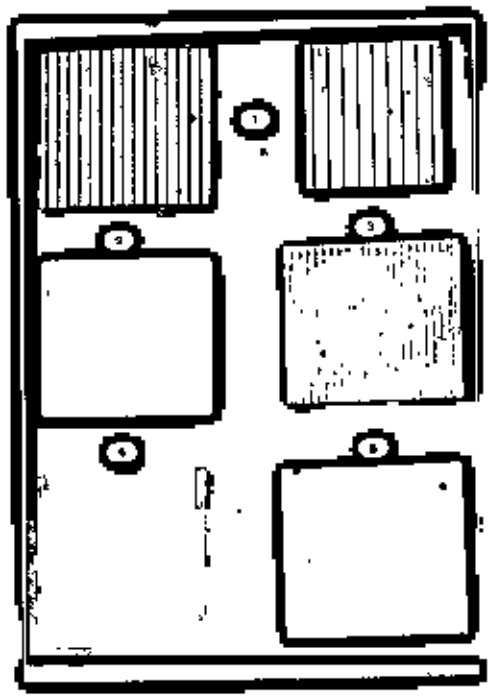
Gummite is prepared by a secret process; it is probably based upon a mixture of asphaltum and some resinous substance.

BATTERY PLATES:

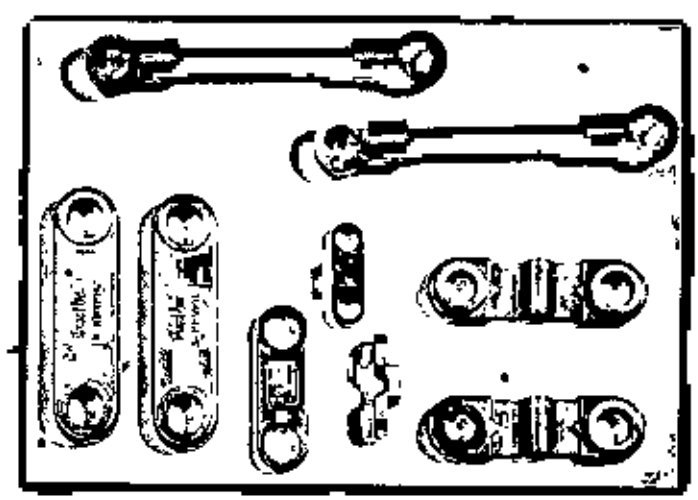
The most extensively used material in storage battery plate manufacture is lead. Pasted plates are made by applying to the grid by hand or by machine a paste consisting of mainly leadoxides, and dilute sulphuric acid. The pasted plates are then dried and then formed electrochemically in a tank containing dilute sulphuric acid. Formation of pasted plates produces oxidation of the lead oxide paste to lead dioxide and its reduction to spongy lead. When formation is completed, the plates are taken out of the acid tanks, ringed in water and dried.

SEPARATORS:

The function of a separator is to prevent metallic contact of adjoining plates of opposite polarity, but they must possess sufficient porosity to allow of good electrolyte conduction between plates. Various materials have been used to make these separators. Modern separators are made from perforated or slotted hard-rubber sheets, treated wood veener, impregnated wood veener, rubber and cotton combinations and glass in rod or spun form.



Separators.



Cell-connectors.

The rubber separators are thin sheets of perforated or slotted hard-rubber and vary in thickness in accordance with the purpose of cell they are used with, the thickness increasing with larger cells. The slotted rubber separators is more recent type than the perforated one. It has been introduced because it can be given greater porosity and yet have substantially the same mechanical strength as the perforated type, especially if ribbed.

Wood separators are made of thin wood sheets threaded through two or more slitted wooden rods or dowels which support the veneers in the correct position between the plates. Wood separators are now being largely replaced by sheets of microporous plastic threaded through slitted rods of polystyerene.

CELL CONNECTORS:

Cell connectors are those parts employed to connect one cell of a group to another. The simplest form of cell connectors is made from a casting of antimonial lead alloy. Lead plated copper connectors have the advantage of greater flexibility and are used as inter-cell connectors for most traction batteries. Connectors are designed to be of low resistance and capable of carrying a current in amperes equal to about 5C, where C is the nominal ampere hour capacity, without any undue voltage drop or heating.

ELECTROLYTE:

A battery when constructed must be filled with dilute sulphuric

acid. The acid must be chemically pure. The electrolyte used in connection with storage battery is dependent upon the type of cell employed, dilution varying with various types (1.200 to 1.300 specific gravity).

Of all these the positive and negative plates and the cell connectors are the only lead bearing constituents. So we charge only these materials into the furnace. This avoids working of the trouble creating ingredients of the battery, helps smooth running of the furnace, increases the capacity and reduces the fuel cost. Although this incurs an increased labour cost, it is more than repaid by smooth working, less fuel cost and less pollution of the atmosphere.

The behavior of the individual ingredients composing the condemned battery plates are as follows :

LEAD OXIDE:

This occurs in two forms - massicot and litharge. Litharge is obtained on a commercial scale by cupeling refined lead and collecting the oxide as skimming or fumes. The melting point of litharge is 883°C. It is volatile in air below 900°C. It is a good conductor of electricity when molten.

Towards acid forming materials litharge is a strong base, quickly corroding them by forming lead silicates. It is an excellent flux forming fusible compounds with oxides that are infusible alone, such as CaO, MgO, and Al_2O_3. These bases do not always enter into chemical combinations with PbO, but are

simply held in fused solutions by an excess of litharge.

Litharge readily gives up its oxygen. Sulphur, tellarium, arsenic, copper, zinc and iron are wholly or partly oxidised when melted with litharge, the oxides either being volatalised or slagged by the surplus of litharge.

Reduction of PbO by carbon begins at 400 to 500°C and is vigorous at 700°C. Reduction by carbon monoxide begins at 160°C and by hydrogen at 235°C. Heated to bright redness with lead sulphide, in the proportion of two molecules of litharge and one of sulphide, all the lead in both compounds is reduced to metal and SO_2 is evolved.

$$PbS + 2PbO = 3Pb + SO_2 + heat.$$

LEAD-PEROXIDE:

This is a powerful oxidising agent detonating with phosphorous. It is used in the manufacture of matches and in storage batteries in which the latter is repeatedly destroyed and reformed during the operations of discharging and charging.

LEAD-SULPHIDE:

This occurs in nature as galena and can be antificially prepared by melting sulphur and lead. PbS melts at 1120°C to a thin fluid which penetrates the fire-bricks of the furnace. It volatalises at temperatures below its melting point.

$$PbS + Fe = Pb + FeS.$$

In the smelting practise the decomposing of lead sulphide is never complete. It is customary to calculate the iron necessary for the decomposition of PbS in accordance with the reaction.

$$Fe + PbS = Pb + FeS.$$

If less iron is added, the resulting matte remains too rich in lead, while if an excess is supplied it simply goes into solution in the PbS - FeS matte. In addition to having the correct amount of iron present to decompose PbS, it is important to have the temperature as high as possible within reasonable limits.

LEAD-SULPHATE:

This occurs in nature as anglesite and is formed in roasting PbS and in precipitating lead-salts with sulphuric acid. It is one of the most stable sulphates of heavy metals, remaining unaltered at a bright red-heat. At 800 to 1000°C it dissociates, fusion also occuring between 950° and 1000°C.

Carbon and carbon monoxide reduce lead-sulphate to PbS with the formation, also of Pb and SO_2. This double reaction explains the disappearance of S and SO_2 in the reducing fusion of lead blast-furnace.

REACTIONS BETWEEN PbO, PbS and $PbSO_4$:

Intimate mixtures of these compounds react in accordance with the reactions

$$PbS + 2PbO = 3Pb + SO_2$$

$$PbS + PbSO_4 = 2Pb + 2SO_2$$

Except for the fact that the gaseous product SO_2 is withdrawn from the furnace as fast as it is formed, both these reactions would reverse and equilibrium would result. If there is an excess of PbS or PbO over that called for by the equation the excess remains unaltered. If there is an excess of $PbSO_4$ part or all of the lead is obtained as PbO.

$$PbS + 3PbO = 3Pb + PbO + SO_2$$

$$2PbS + 2PbO = 3Pb + PbS + SO_2$$

$$PbS + 2PbSO_4 = Pb + 2PbO + 3SO_2$$

$$PbS + 3\ PbSO_4 = 4PbO + 4SO_2$$

Frequently the blast furnace process is regarded as a simple process, where as it is actually full of complexity. The complexity is aggravated by the fact that the actual conditions within the furnace are either unknown or very difficult to determine. The blast furnace process is indeed composed of many delicately balanced reactions many of which are interdependent.

FUEL:

Fuel in a blast furnace has a dual role. It is a heat producer and a reducing agent. The fuels which are employed fall into 2 classes - natural fuel and prepared fuel. The natural fuels - anthracite and bituminous - are of historic rather than economic interest.

The prepared fuels are coke and charcoal. Although coke is practically the universal blas furnace fuel, charcoal is still used at a few plants. At most plants, however, coke is employed

as the fuel and the quality of the coke used has a fundamental effect on the operation and output of the furnace.

For the successful operation of a blast furnace, four characteristics of fuels are of fundamental importance:

1. Cell Structure or Porosity:

A dense structure in the coke hinders the intimate contact between the carbon of the coke and the oxygen of the blast, thereby retarding rate of combustion. The rate at which the coke is burnt and therefore the caloritic effect per unit of time, varies with:

(a) the area of the fuel exposed to the blast.
(b) the affinity of the particular type of carbon for oxygen.
(c) the temperature and pressure of the blast.

It is therefore obvious that an open well-developed structure exposing the maximum area of carbon to the blast, is desired. The physical standard by which blast furnace coke is generally measured, besides hardness and resistance to abbrasion is its porosity.

2. Resistance to Abbrasion:

A coke that breaks down easily into brese will adversely effect the operation of a blast-furnace. The height of a modern blast-furnace is controlled very largely by the strength of coke available.

3. Reactivity or Combustibility:

The reactivity or combustibility of coke may be defined as the rate of reaction between the coke and oxygen. Reactivity is not directly related to the rate at which the air is supplied and other factors. The reactivity of a coke, however, does indirectly affect the intensity of combustion within the furnace.

4.. Purity:

The influence of the ash content of coke in blast-furnace reaction can be appreciated when it is realised that 1 pct. ash requires 2 pct. coke for its removal.

FLUXES:

In addition to the ore and fuel fluxes are an important part of a blast-furnace burden. The purpose of such fluxes are to convert the gangue of the ore and the ash of the fuel into a fu fluid slag. The selection of the proper flux or fluxes is essential for efficient and economic operation of the process. The better the flux the greater is the removal of gangue per unit weight of flux. This gives a good slag and smooth running of the furnace, with a lower loss of lead in the slag. The most suitable fluxes in this case is CaO and FeO.

The four slag forming constituents concerned are FeO, CaO, SiO_2 and PbO. Of these lime has the greatest tendency to form slag with SiO_2 and PbO the least. Excess lime however will have a

tendency to combine with PbO, The presence of FeO is needed on the assumption that it will displace at least partially the PbO that may get entangled in the slag and render it available for reduction to metallic lead. Finally the addition of FeO will form a ternary addition and will reduce considerably the melting point of slag. A charge must therefore be used which will give a fluid slag at fairly low temperature. It has been found that these slags usually contain 29 to 38, per cent SiO_2, 24 to 45 per cent FeO, and 14 to 24 per cent CaO.[10]

Chapter 6

CHARGE CALCULATIONS

BLAST-FURNACE CALCULATION[11]

The smooth working of a blast-furnace is very much dependent on correct burdoning. It may be remarked that calculation of charges is not a regular or routine part of furnace operation.[11] When the furnace is running regularly, minor adjustments of charge are often made simply on observation. For example, if it is found that the slag is becoming a little too basic, the furnace-man simply increases a little the proportion of a silicious ore or reduces the proportion of a basic flux. If it becomes necessary to change to a new ore, which contains, say more silica than one previously used, the flux may simply be increased by an estimated amount. In starting a new furnace it may be possible to make up the charge by simply making it similar to one previously used. In some cases, however, better results might be obtained by calculation than by practical 'trial and error' method.

A charge similar to that used in battery-plate smelting blast-furnaces has been used. Some calculations, however, has been made to compare these figures and those obtained from the existing furnace operation data.

The raw materials used have the following composition:

Battery Plates:

$PbSO_4$	= 38	per cent
PbO_2	= 19	"
Pb	= 34	"
Sb	= 1.54	"
Moisture etc.	= 7.46	"

Lime Stone:

$CaCO_3$ = 98 per cent

SiO_2 = 5 per cent

Coke:

Carbon = 80 per cent

SiO_2 = 9 "

Ash = 8 "

Moisture = 3 "

DETERMINATION OF COKE REQUIREMENT:

There is no satisfactory method of calculating the fuel required. It is however desirable to have some method of estimating the approximate coke consumption or requirements, which can subsequently be adjusted. Each hundred pounds of charge requires 20 lbs. of coke for the reduction for the formation of the slag.

DETERMINATION OF FLUX:

The amount of flux required to form the slag depends on the basicity of the slag produced. Basicity is the ratio$(CaO + FeO)/SiO_2$. For our purpose a basicity of 1.6 is adopted. Therefore the available base in the limestone will be ;

$CaCO_3$ = 98 per cent

CaO = 98 x .56

= 54.2 per cent.

Acid in lime stone = 5 per.

This multiplied by basicity gives the CaO equivalent.

∴ CaO equivalent = 5 x 1.6 = 8 .

Therefore efficiency of lime stone = $\frac{100}{55.2-6}$ = 2.2

Now 100 lbs plate requires 20 lbs coke which will require the following flux to deal with the ash content :

SiO_2 = 20 x .08 = 1.6

multiplied by basicity 1.0 = 2.56

Bases present = .02 x 20 = 0.4

Therefore CaO required = 2.56 - 0.4

= 2.16

2.16 x 2.2 = 4.75 lbs/100 lb charge.

Therefore lime/100 lbs charge = 5 lbs.

Iron-Oxide:

In practice decomposition of PbS is never complete in blast-furnace operations. It is customary to add Fe_3O_4 in accordance with the reaction PbS + Fe = FeS + Pb. As PbS is reduced by PbO, with the formation of Pb and SO_2 it has been assumed that 20 pct. PbS is reduced by Fe and hence the amount of Fe_3O_4 charged should be :

$$2PbSO_4 + 3C = PbS + Pb + CO + SO_2$$

$$2PbSO_4 + 3CO = PbS + Pb + CO_2 + SO_2$$

In both the cases 2 x (207 + 32 + 64) = 606 lbs of sulphate produces 239 lbs of sulphide. Of this 80% is assumed to be reduced by Fe,

according to the reaction

$$PbS + Fe = Pb + FeS$$

which means 239 lbs of PbS requires 56 lbs of Fe.

The charge contains 38 lbs of sulphide which produces $\frac{239 \times 38}{606} = 15$ lbs of PbS, of which 3 lbs is reduced by FeO. This is reduced by 0.7 lbs Fe. This is contained in $0.7 \times \frac{232}{168} = 1$ lb Fe_3O_4.

The charge used was as follows:

Battery Plate	= 100lbs
Coke	= 20 lbs.
Lime	= 4 lbs
Iron Oxide	= 2 lbs.

A typical blast-furnace charge[12] obtained from a plant smelting battery plates consists of :

Battery Plates	= 650 lbs.
Coke	= 70 lbs
Lime stone	= 20 lbs
Iron ore(Fe_3O_4)	= 10 lbs
Dross & Matte	= 150 lbs
Dump slag	= 120 lbs

A higher coke charge has been used because it is of lower grade than those used in western countries. No dross and matte were produced and hence were not charged in latter operations because of very negligible amount of copper. As the amount of slag produced was very small in amount, it could not be charged them in each subsequent operation. However, all the slag obtained from earlier operations were charged in the last operation.

Chapter 7

THE SMELTING OPERATION

The Charging-door

Charging being done

CHARGING

Distribution of the charge in the furnace is one of the most important factors in the regular working of the blast-furnace. If the charge is not properly distributed these areas containing the coarse material offer less resistance to the passage of the blast which results in higher temperature in these parts and a tendency for the charge to descend in an irregular manner. There are many automatic and semi-automatic devices for getting a smooth distribution of the charge.

A very small furnace which smelted battery plates for several times only was used and it was unnecessary to install any mechanised system. This was done manually. The raw materials were loaded into buckets at the base of the furnace from the main stock and then raised up to the charging platform.

The entire charge for one operation was divided in several parts. After the first layer of plates was charged, proportional amount of fluxes were charged, so that intimate contact between the charge and flux can be established. This was followed by a layer of coke. Care was taken to ensure that the distribution was uniform.

The other parts of the charge were charged in the same way, layer by layer.

PHYSICAL APPEARANCE AFTER CHARGING:

Just after the charging was complete, the blower was turned on. Forcing of air in the tuyere zone of the furnace speeded up the rate of combustion and within minutes dense smoky fumes began to come out. This has a somewhat suffocating effect and odour mainly due to the presence of sulphuric acid fumes. Small amounts of separators which might have come along with the charge, burn in the furnace and contributes further to this disagreeable

odour. This continued for nearly 20 minutes. As the process continued the fine gradually turned white but traces of the odour was there. This is due to the decomposition of the lead sulphate of the battery plates leading to the formation of SO_2. Some amount of lead oxide also volatalises giving rise to the white appearance of the gas.

Yellowish flames including the flames of fire became visible when another half an hour was passed. This continued throughout the operation.

A very small amount of PbO was collected near the top of the furnace. This is due to the condensation of PbO fumes at that place.

BLAST-FURNACE REACTIONS: [13]

The air for combustion of the coke enters the furnace through tuyeres situated just above the hearth. Immediately the air and coke meet, combustion takes place, with the formation of carbon dioxide ultimately leading to the formation of CO in the presence of excess of red hot coke.

At the high temperatures prevailing in the combustion zone and in the bosh immediately above this zone, little or no CO_2 is left, the carbon being converted to 100% CO. Any CO_2 formed in this zone is immediately converted into CO by reaction with the carbon of the coke.

$$C + CO_2 \longrightarrow 2CO.$$

As the gases ascend the shaft there is an increased tendency for the production of CO_2, since the gases are now encountering more and more unreduced oxides, and because the velocity of the reaction $C + CO_2 \rightleftharpoons 2CO$ is decreasing, due to decreasing temperature.

At about 800C the zone in which limestone is dissociating, and where a considerable amount of oxide is reduced, considerable quantity of CO_2 are

formed. This tendency for the production of CO_2, increases as the gases pass up the stack, due to the reduction of the oxides and to the fact that the velocity of the reaction;

$$C + CO_2 \rightarrow 2CO,$$

is so reduced that it is unable to dispose off the CO_2 formed by these reactions.

This reaction $C + CO_2 \rightarrow 2CO$ is a reversible reaction of considerable importance in the blast-furnace and it is affected by the following factors :

1. The reduction of CO_2 by C with the production of CO absorbs 14,650 less 2 X 4430 = 5660 BTU per lb. of C. Therefore the reaction is endothermic and the production of CO is favoured by a high temperature. In otherwords, the velocity of the reaction $C + CO_2 \rightarrow 2CO$ is reduced as the temperature falls. Conversely, the velocity of the reaction $2CO \rightarrow CO_2 + C$, which is exothermic, increases as the temperature falls.

2. Increased pressure for any reason favours the production of CO_2 owing to the volume change which takes place during the reaction.

3. The direction of the reaction is also effected by the concentration of the reacting constituents. An increase in the percentage of CO_2 will tend to make the reaction proceed thus :

$$C + CO_2 \rightarrow 2CO.$$

The increase of CO_2 higher up in the furnace is probably due to dissociation of lime-stone and due to reduction of oxides. Inspite of the gradual increase of carbon dioxide in the gases as we go higher and higher up gas the furnace, the character of the exit gases will be definitely reducing in

nature and the ratio $CO:CO_2$ will be more than 1.

For many years it was generally accepted that this ratio must not be allowed to fall below 2, if satisfactory reducing conditions were to be maintained in the furnace. It has, however, been demonstrated in many plants that furnaces can be successfully operated for long periods with a CO/CO_2 ratio of 1.35 or even less. In general, the lower ratios are obtained with higher blast pressures. It is probable that good reduction can be obtained because the CO_2 formed is quickly removed from the reaction phase by the more rapid flow of the ascending gases. This would reduce the concentration of CO_2 in the reacting zone.

When considering the reactions between ascending gases and descending charges, the velocity with which the reactants move must be borne in mind. The great difference in the velocity of the two column prevents equilibrium being established.

It has been found that from economy's point of view, it is important that the CO/CO_2 ratio is kept as low as possible, consistent will good reduction. A high ratio results in a higher coke consumption.

The nitrogen in the gas is practically inactive. Although hydrogen is a strong reducing agent, it appears to play little or no part in the reduction process in the blas furnace. The percentage of hydrogen in the gases varies with the different seasons of the year, and the humidity of the atmosphere.

THE DESCENDING COLUMN OF SOLID MATERIALS: [14]

The velocity of the descending column of raw-materials is much slower than that of the ascending column of gases. As these solids descend, they are gradually preheated, prepared and reduced, so that on reaction the lower

part of the bath they should exist as reduced antimonial lead, partly fluid slag and coke. The coke is practically unchanged till it reaches the tuyere zone, when the combustion takes place. The metal as soon as it is reduced drips through the tuyere zone to the hearth, from which it is tapped as required.

At the top of the furnace the moisture, any combined water and fumes of sulphuric acid is expelled.

The reduction of PbO by carbon monoxide commences at 150°C and is accelerated as the temperature increases upto about 1000°C beyond which point it falls off rapidly. The carbon of the coke begins to act reducingly at about 400°C and increases as the temperature rises. The lead thus liberated trickles down and collects at the hearth. The reduction of lead oxide by CO should be accomplished in the higher and cooler parts of the furnace where the carbon dioxide formed by the reaction is not likely to be decomposed by hot carbon. In otherwards, this reduction by carbon monoxide should be completed before a 'red-heat' zone is reached.

Reduction of PbO by C begins at about 450°C and is vigorous at about 700°C. It will be found that the direct reduction of the oxide is endothermic and is therefore favoured by a high temperature. It follows that direct reduction takes place at the hotter zones of furnace.

Both carbon and carbon monoxide reduces $PbSO_4$ to PbS, with the formation also of Pb, and SO_2. This double reaction explains the disappearance of S and SO_2 in lead blast-furnace. At 800°C to 1000°C, $PbSO_4$ dissociates. Fe_3O_4, charged as a flux, has a decomposing effect on $PbSO_4$.

In the neighbourhood of 600°C, the dissociation of lime stone commences

thus :

$$CaSO_3 \rightarrow CaO + SO_2 - 811 \text{ BTU per lb. of } CaSO_3$$

This reaction which is endothermic, is accelerated by a rising temperature and is practically completed at a temperature of 600°C. Reacting with $PbSO_4$ some CaO is sulphated.

$$PbSO_4 + CaO = CaSO_4 + PbO$$

PbS melts at 1135°C to a thin fluid which penetrates the fire-bricks of the furnace. It volatilises at temperatures below its melting point. In smelting practice decomposition of PbS is never complete. Intimate mixtures of PbS, PbO and $PbSO_4$ react in accordance with the following reactions :

$$PbS + 2PbO = 3Pb + SO_2$$

$$PbS + PbSO_4 = 2Pb + 2SO_2$$

Except for the fact that the gaseous product SO_2 is withdrawn from the furnace as soon as it is formed, both these reactions would reverse and equilibrium would result.

If there is an excess of PbO or PbS over that called for by the reaction the excess remains unaltered. If there is an excess of $PbSO_4$ part or all of the lead is obtained as PbO.

$$PbS + 2PbO + heat = 3Pb + SO_2$$

$$2PbS + 2PbO + heat = 3\ Pb + PbS + SO_2$$

$$PbS + 2PbSO_4 + heat = 3PbO + Pb + 3SO_2$$

$$PbS + 3PbSO_4 + heat = 4PbO + 4SO_2$$

PbS is also reduced by Fe obtained from oxides of iron. It is customary to calculate the amount of iron necessary for the decomposition. If less

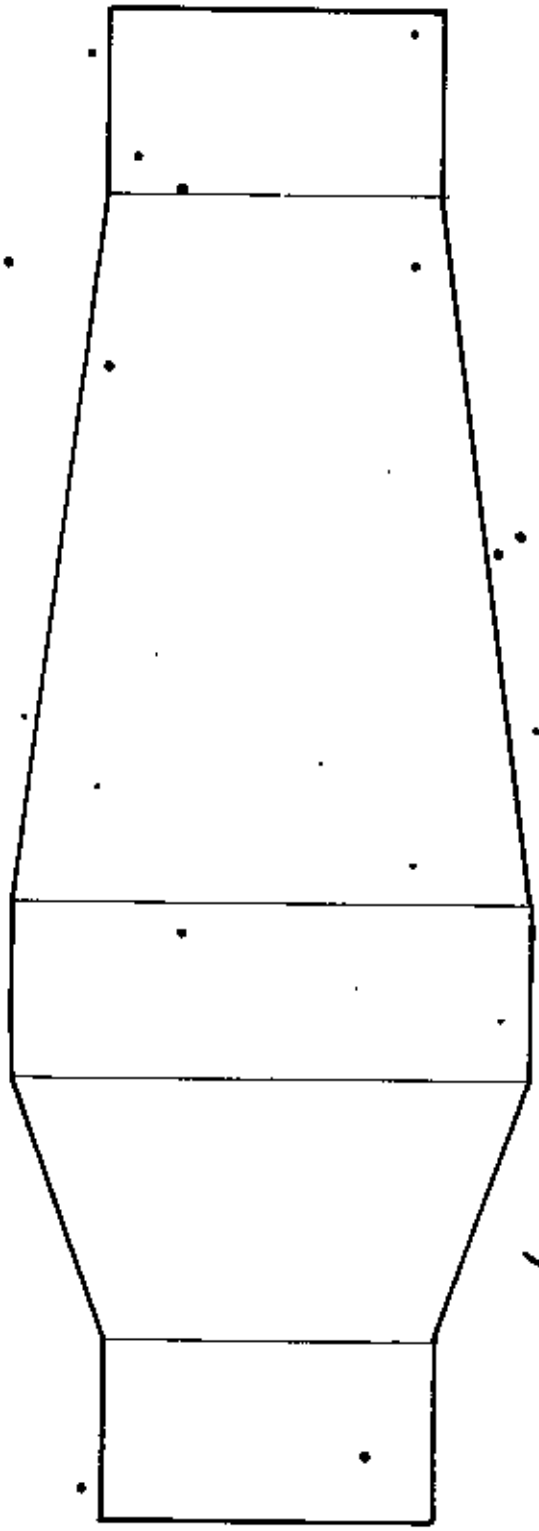
iron is added the resulting matte remains too rich in lead and if too much iron is added it simply goes into the solution in FeS - PbS matte. It is also necessary to maintain the temperature as high as possible.

To be good for lead smelting slags should melt at 1150 - 1250°C. Too low melting slags would melt and trickle down into the crucible before the lead-oxide in them has had time to be reduced; too high melting slags would involve increased fuel consumption.

The principal role of slags is to withdraw the impurities mainly silica. Slags consisting mainly of CaO and SiO_2 are heavy and separate from the matte with difficulty.

Iron-oxide added as a third component reduces the specific gravity of the slag and enhances the reduction of lead by increasing the activity of PbO in the slag.

In the figure on the next page an attempt has been made to summari these reactions in graphical form, showing the zones in which the various reactions take place. The actual contour of lines of demarkation between the zones will depend on the type of distribution in the furnace. The distribution of the burden in the furnace affects the gas velocity, the carbon dioxide content and the temperature prevailing in the different parts of the furnace and these factors control the reactions taking place.



$PbO + CO \rightarrow Pb + CO_2$ 250°C

$PbO_2 + 2CO = Pb + 2CO_2$

$PbO + C = Pb + CO$ 400°C

$PbO_2 + 2C = Pb + 2CO$ 800°C

The same vigorous 700°C
$CaCO_3 = CaO + CO_2$

$PbSO_4 + CO = Pb + PbS + CO_2 + SO_2$ 800°C

$PbSO_4 + C = PbS + Pb + CO + SO_2$ 1000°C

$PbSO_4 + PbS = Pb + SO_2$ 1100°C

$PbO + PbO = Pb + SO_2$

$PbS + Fe = Pb + FeS$

$CO_2 + C = 2CO$

$C + O_2 = CO_2$ 1200°C

OPERATION DATA

	CHARGE					PRODUCT	
Operation No.	Plates lbs	Coke lbs	Lime lbs	Iron Oxides lbs	Dump slag & skimming	Lead contained lbs	Lead obtained lbs
1	270	30	12	-	-	128	68
2	270	30	8	1.5	-	128	92
3	270	35	8	4	-	125	80
4	180	25	6	2	-	100	88
5	100	20	.5	1	-	48.4	48
6	200	120	25	20	75	328*	328
TOTAL	1290	280	62	28.5	75	838.4	680

* The metal content of the slag and skimmings has not been included in this figure.

As the cell connectors contained antimonial lead in the metallic form, they were simply melted in a crucible.

Total weight of lugs was 180 lbs from which 135 lbs of metal could be obtained as castings. The rest were non-metallic impurities and skimmed off.

This is actually very difficult to arrive at a conclusion regarding the effect of the fluxing material on the efficiency of the blast-furnace from these data. They are very inadequate. However, it can be said that Fe_3O_4 has to be added to give good output. This oxide increases the activity of PbO in the slag makes it free for subsequent reduction. FeO has got a greater affinity than PbO for silica to form silicates.

But there is probably some adverse effect on efficiency if the quantity of FeO exceeds the optimum amount. They, when present in larger amount than that called for by the reaction PbS + Fe = Pb + FeS, have a tendency to form a PbS - FeS matte, thereby reducing the output of lead.

Future investigations may be directed to find out the effect of FeO on the running of a lead-blast furnace.

Chapter 8

DISPOSAL OF PRODUCTS

Tapping of the metal.

DISPOSAL OF PRODUCTS:

Lead:

The antimonial lead resulting from the smelting operations collects in the hearth of the furnace and is tapped out through the tap-hole. The molten metal is collected in a laddle. The metal as it flows out from the furnace; is at red heat and contains 2 - 5 pct. antimony (our analysis showed an antimony content of 3.47 pct.) As it cools non-metallic impurities and some oxide floats on the surface and is skimmed off with a considerable amount of entrained lead and lead oxide. The lead is then cast into metallic molds into small slabs and allowed to solidify. The metal produced in this case contained 3.47 pct antimony. Lead-antimony alloys containing 6 - 10 pct antimony are used for storage battery plates and a similar material is used for toy soldieres and ornamental castings. The weighty filling of bullets for small arms ammunitions consists of lead-antimony alloy containing 2 - 5 pct antimony. So we see the metal obtained by smelting can be used as such or by using small additions for many day to day needs. Some more per cent of antimony can added and the resulting metal used as white metal. Type metal can also be made by proper additions of antimony and tin.

Pure lead, however, can be produced by blowing the molten metal by oxygen thus oxidising the antimony. This is possible because antimony oxidises more rapidly than lead.

But it is cheaper to make suitable alloy and use it.

Slag:

This consists mainly of silicates of iron and lime. It generally comes

out of the slag-hole. But the bricks used were of lower quality and could not allow full use of the hearth. This flowed out of the tap-hole after the metal. The slag was not very fluid and so was found to contain a large amount of entrained lead in the form of small balls. The slag loss was considerable, however, actual analysis of slag in the laboratory revealed that only trace amount of lead was present in the combined form in the slag.

The slags of All the previous charges were charged together with the plates in the last charging. The slag of the last smelting operation weighed 150 lbs and were thrown away.

FUME AND FLUE-DUST

A considerable amount of lead fume is produced where the metal is heated above red-heat, and it is accompanied by still more volatile antimony. Fume losses in this case, has been approximated from the knowledge of the similar losses in the prevalent lead industries of similar nature.

Treatment of Fue and Flue-Dust:

A considerable amount of lead-fume is produced in operations where the metal is heated above red-heat. In blast-furnace smelting, a large amount of lead. (Approximately 60 lbs of flue-dust is produced in treating 1 ton battery plates, which contain about 63 pct lead and 5 pct antimony).[15]

The earliest method for collecting dust or fume was to enlarge the flues to form a dust chamber which caused a lowering of gas velocities and thus allowed much of the dust to settle out. The dust chambers were often equipped with hopper bottoms for removal of settled materials. The finer particles were not precipitated, and although considerable coarse dust is

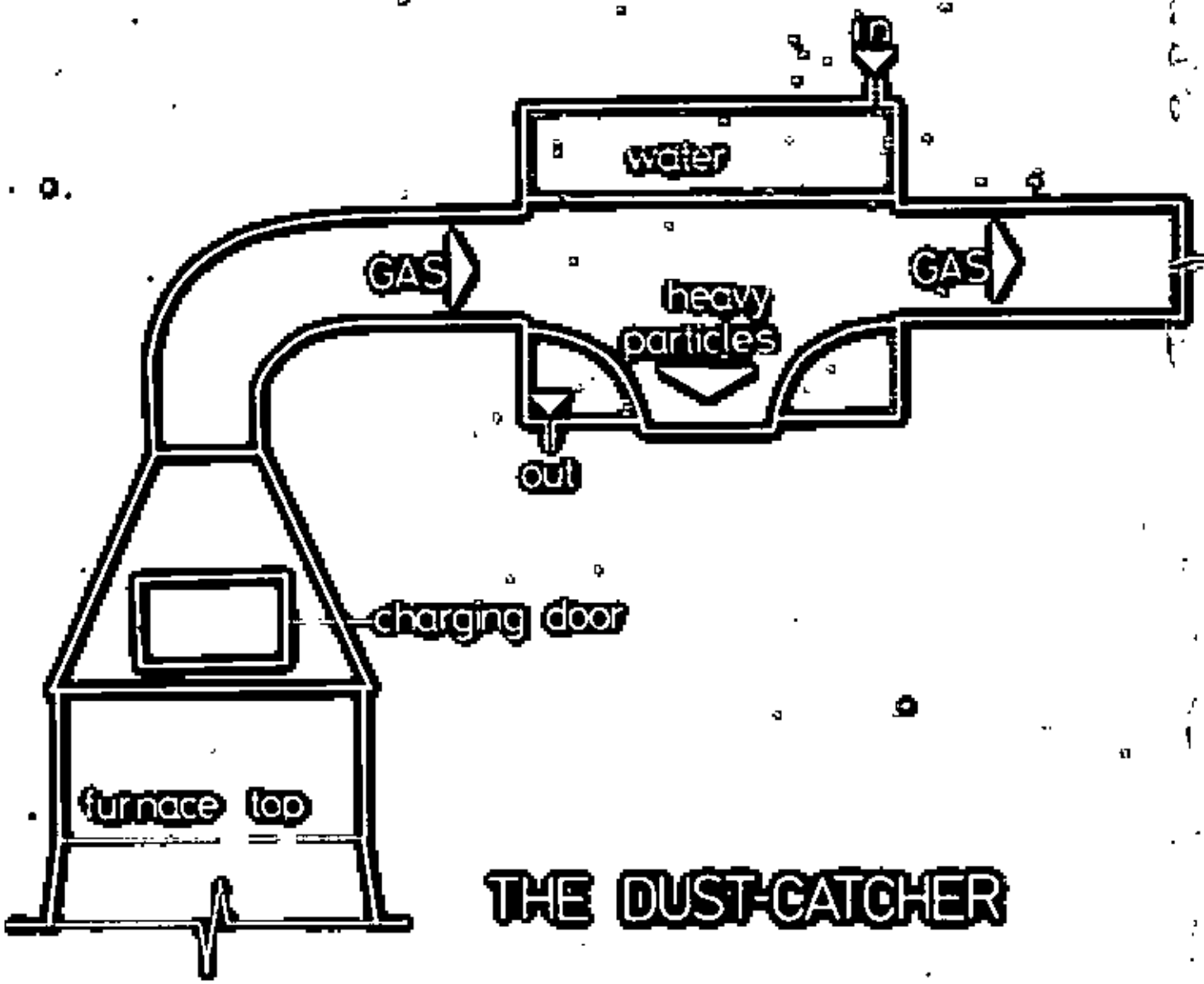
still recovered from smaller flue systems, more effective methods have become common. Of all the methods, (a) bag house and (b) cottrell precipitator are commonly practised in lead smelting.

The aim of the investigation has been to see the possibility of recovering lead from battery plates. Moreover the construction of both the bag-house and cottrell precipitator are complex. Just to show that some lead is carried away by flue-dust and that it can be recovered, one dust catcher which is very simple in principle was used. This however reduced the pollution of the atmosphere by the fumes. The out-coming gas and flue-dust was made to pass to a large chamber through a pipe. Due to the reduction in velocity of the gas and due to the cooling effect of the circulating water the coarser dust particles settled down and was collected in a bag suspended at the mouth of an opening at the bottom, while the gases and the finer particles passed on and escaped to the atmosphere.

The gas and water inlet are placed on the opposite ends, so that gases passing through gradually come in contact with cooler water. This ensures better cooling. The sketch may be helpful to get an idea of what actually happens. (See page 804)

Only the last operation was done with the dust catcher. Nearly 2 lbs. of particles was collected in the bag. As it did not melt even at 340°C it was either PbO or $PbSO_4$. But only a very small part of it dissolved in ammonium acetate solution, leading to the conclusion that it was mainly PbO.

This proves that a considerable amount of lead is vaporised during the operations and that they can be recovered by suitable devices.



THE DUST-CATCHER

Chapter 9

ECONOMY STUDY

COST ANALYSIS OF A PLANT PRODUCING 1.5 TONS OF LEAD PER DAY

DIRECT COST

A. Furnace and Accessories

1.	a) Steel sheet	Taka 3000.00
	b) Shearing of sheets, shaping and welding including labour	Taka 3000.00
	c) Base plate including machining	Taka 500.00
	d) Foundation and Erection	Taka 1000.00
	e) Bricks	Taka 3750.00
		Taka 11,250.00
2.	a) Charging platform	Taka 3000.00
	b) Pulley arrangement for lifting the charge to the platform	Taka 1000.00
		Taka 4,000.00
3.	Bag-house construction	Taka15,000.00
4.	2 Hp Motor coupled with an electric blower	Taka 6,000.00
6.	Electrification	Taka 5,000.00
		Taka 26,000.00
B. 1.	Building (Including services) 2000 sft.	Taka 100,000.00
2.	Service facilities	Taka 10,000.00
C.	Land 15,000 sft.	Taka 100,000.00

INDIRECT COST

A.	Engineering and Supervision	Taka 10,000.00
B.	Contingency	Taka 5,000.00
		Taka 15,000.00

TOTAL FIXED CAPITAL INVESTMENT

= Direct Cost + Indirect Cost

= Taka 265,250.00

MANUFACTURING COST

A. Direct production cost

i. Raw-materials

a) Battery, 50,000 Nos. @ 15 per piece	Taka750,000.00
b) Coke, 250 tons @ Taka 20,000.00 per 100 tons	Taka 50,000.00
c) Lime-stone 30, tons @ Taka 800.00 per ton	Taka 25,000.00
d) Iron-ore 20 tons @ Taka 250.00 per ton	Taka 5,000.00
e) Carrying cost @ Taka 200.00 per ton	Taka160,000.00
	Taka 990,000.00

B. Operating labour:

Foreman	1	Taka 6,000.00
Labourer	6	Taka 9,600.00
		Taka 15,600.00

3.	Direct supervisory and clerical labour	Taka 5000.00
4.	Maintenance and repairs	Taka 6000.00
5.	Power	Taka 1000.00
		Taka 12,000.00
B.	Fixed Charges	
	1. Depriciation	Taka 12,000.00
	2. Local taxes	Taka 6,000.00
	3. Insurance	Taka 2,000.00
		Taka 20,000.00
C.	Plant Overhead	Taka 12,000.00
D.	General Expenses:	
	A. Administrative Expenses:	
	Manager 1	Taka 12,000.00
	Engineer 1	Taka 12,000.00
	2. Financing and interest	Taka 12,500.00
	3. Laboratory charges	Taka 5,000.00
	4. Distribution and sales	Taka 12,000.00
		Taka 53,500.00

TOTAL PRODUCTION COST

A.	Direct production cost	Taka 1,017,600.00
B.	Fixed charges	Taka 20,000.00
C.	Plant Overhead	Taka 12,000.00
D.	General Expenses	Taka 53,500.00
		Taka 1,103,100.00

PROFITABILITY

There are several methods of representing the profitability of a proposed investment. The profitability, in this case, is reported in the simplest method — rate of return on investment.

Sales receipt from 400 tons of lead = 400 x 2000 x 2

= Taka 1,600,000.00

Therefore, total Gross profit = 1,600,000.00 - 1,193,100.00

= Taka 406,900.00

Total investment = Taka 265,250.00

Therefore, rate of return on investment

$$\frac{406,900}{265,250} \times 100 = 150 \text{ per cent.}$$

The prospect of the investment is brighter when consideration is taken of the fact that 6 years of tax-holiday would be allowed by the Government.

CONCLUSION

The profitability study of the investment shows that the prospect of the proposed investment is very bright. However, care should be taken in concluding from the estimates presented. This reports positive results show that further work along this line is worth doing. Making a 'firm design report' is strongly recommended which will contain every detail of proposal, specifications, operating schedule, optimum operation rate and so on.

The American Bureau of Metal Statistics estimates that, the output of secondary lead in 1938 equaled 58.6 per cent of the total production of refined primary lead from domestic and foreign sources in the United States. In the last normal year 1938, a total of 224,000 short tons of secondary lead was recovered.

World War II brought with it an increase in the amount of lead recovered and in 1945 a total of 341,243 tons (short) of lead was produced, valued at $43,000,000.Of these battery plates contained 152,049 short tons [16] of recoverable lead.

The above facts and informations are very inspiring for further work on this subject. Some specific suggestions can be made as follows :

1. The effect of the fluxing materials especially iron-oxide on the recovery may be studied.
2. The temperature may be increased to make the slag fluid and see the results.
3. Effective flue-dust recovery system may be installed.
4. The furnace may be operated continuously for atleast several days to see the effect on recovery.
5. An effective temperature measuring device may be installed and attempts may be made to establish the reactions.

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