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## RECENT IMPROVEMENTS AND TRENDS IN

## LEAD-ZINC EXTRACTION METALLURGY [1]/

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# C O N T E N T S

# RECENT IMPROVEMENTS AND TRENDS IN LEAD-ZINC EXTRACTION METALLURGY

## INTRODUCTION

It is considered beyond the scope of this paper to describe the standard lead and zinc extraction processes. It is therefore assumed that these processes are well known, and the only processes described here are further developments of the conventional processes, or new processes about which comparatively little has been published to date.

## LEAD AND ZINC ORES

The early lead and zinc industry was based on the processing of rich and pure sulphide and oxide ores in which the main constituent was either lead or zinc. Later, mixed lead-zinc ores in which the two components were easily separated by flotation, were used. However, with growing demand for lead and zinc it has become increasingly necessary to utilize complex, fine-grained ores in which the lead and zinc minerals are difficult to separate from each other and from other minerals often present such as pyrite and copper minerals. Also, it has become necessary to use ores containing a wide variety of impurities, often in large amounts. The lead-zinc industry is therefore today faced with the necessity of treating impure ores and concentrates and complex lead-zinc materials.

## METAL QUALITY

At the same time as the quality of ores and concentrates has deteriorated, there has been a continuous increase in metal purity requirements and the lead-zinc extraction industry has had to meet this challenge to respond to an increasingly demanding market. The following examples

illustrate this trend.

For the purest grade of refined lead in the United States a maximum bismuth content of 0.05 % used to be specified and is still the official specificiation, but some large customers now specify as low as 0.0025 %.

Similarly, purity requirements for zinc used for continuous galvanizing are steadily increasing in the United States. At the present time, a lead content of less than 0.1 % Pb is usually specified, whereas not so many years ago 0.2 to 0.4 % Pb were generally accepted by the steel industry. In the case of cadmium, specifications now call for less than 0.03 % Cd in most cases, and less than 0.02 % Cd in some cases.

Rolling zinc specifications in the United States are now as follows:

| | |
|---|---|
| Tin | less than 0.0001 % |
| Aluminum | less than 0.0003 % |
| Indium | less than 0.003 % |

In Western Europe, purity requirements are generally less strict. For example, the limit for cadmium in zinc for continuous galvanizing is usually now 0.05 % in Great Britain, and the tin limit in rolling zinc is 0.003 %. However, Western Europe will undoubtedly follow the North American trend.

Quality requirements for Special High Grade (diecasting grade) zinc have also been raised in recent years as shown by the following specifications:

| | United States | | Great Britain | |
|---|---|---|---|---|
| | previous | present | previous | present |
| Zinc, minimum | 99.99 | 99.99 | 99.99 | 99.99 |
| Lead, maximum | 0.006 | 0.003 | 0.006 | 0.003 |
| Cadmium, maximum | 0.004 | 0.004 | 0.004 | 0.002 |
| Tin, Maximum | 0.003 | 0.001 | 0.003 | 0.001 |
| Iron, maximum | 0.005 | 0.003 | 0.005 | 0.003 |
| Indium, maximum | not specified | | | 0.001 |
| Thallium, maximum | not specified | | | 0.0005 |

## DEVELOPMENT OF THE LEAD-ZINC INDUSTRY

Early processing of lead ores on an industrial scale was based on Scotch or Newman hearth and blast furnace smelting; the latter is still by far the most important lead smelting method in the world today. All lead smelting methods produce a crude metal known as lead bullion which since early times was refined to commercial lead by chemical treatment of the liquid bullion, this being facilitiated by the low melting point of lead. Most impurities can be efficiently removed, and valuable byproducts such as silver and gold recovered from lead in this fashion. However, bismuth, which occurs in certain lead ores, could not be removed by the early fire refining methods and the electrolytic lead refining process was therefore developed for the treatment of lead bullion with high bismuth content. In recent years fire refining methods suitable for high bismuth lead have also been developed but electrolytic lead refining is still of interest as the method which produces refined lead of the highest purity.

The first industrial smelting method developed for zinc ores was horizontal retorting. This is a batch process requiring much labour under uncomfortable working conditions and producing an inferior quality of zinc by present standards. In the period from 1916 to 1930 three other zinc processes were developed: the electrolytic process simultaneously by Cominco in Canada and by Anaconda and Bunker Hill in the United States, the vertical retort process by New Jersey Zinc Company in the United States and the electrothermic process by St. Joseph Lead Company, also in the United States. All these processes use less labour and produce purer metal than the original horizontal retort process. All three processes have found wide acceptance throughout the world, in particular the

electrolytic process which made it possible to utilize electric power for zinc production in areas where carbonaceous materials are deficient or expensive. The electrolytic process also made it possible, for the first time, to produce on an industrial scale the high purity zinc which made possible the development of the zinc diecasting industry and continuous galvanizing in the period during the two world wars. So successful has the electrolytic process been that it now accounts for approximately 60 % of the world's zinc production. At the same time it became imperative to improve the quality of thermally produced zinc in order for it to compete with electrolytic zinc. This was achieved by the refluxing method developed by New Jersey Zinc Company in the 1930's, which is now in general use throughout the world for upgrading zinc produced by all thermal processes.

Lead and zinc sulphide ores must be roasted for sulphur removal before smelting. Until the last war this was done by sintering, mostly on Dwight-Lloyd machines, in the case of lead concentrates, and on hearth roasters, mostly Herreshof type multi-hearth roasters, in the case of zinc concentrates.

This was then, in broad outline, the state of lead and zinc processing, around 1950.

## RECENT TRENDS IN LEAD-ZINC TECHNOLOGY

Lead smelting and refining technology has remained basically unchanged. In other words, even the most recent lead plants are still based on conventional sintering, blast furnace smelting, and in most cases, fire refining. However, these conventional processes have been improved in recent years and development work is proceeding on various new processes which might radically change lead smelting technology in the future.

In the case of zinc, much greater changes have occurred in recent years. These include important changes in zinc roasting technique and further improvement of all the already mentioned zinc smelting methods.

However, the most fundamental technological development in recent years is the Imperial smelting process which for the first time has made it possible to produce lead and zinc from a single unit, thereby making it possible to process complex lead-zinc raw materials which cannot be treated efficiently by separate lead and zinc processes.

## LEAD SMELTING

Improvements in recent years have been mainly directed towards better materials handling methods, mechanization and process control in connection with conventional sintering and blast furnace smelting. In addition to this there have been some significant developments which should be mentioned.

### Lead sintering

Conventional sintering of lead concentrates on Dwight-Lloyd machines was carried out by drawing air from above through the sinter bed. Because of the low melting point of lead compounds, and also because lead oxides, sulphides and sulphates inter-react to produce metallic lead, this practice resulted in molten metallic lead and lead compounds attacking the grate and often dripping into the windboxes beneath the sinter strand. To improve sintering conditions and lower maintenance costs the updraft sintering method was developed by Broken Hill Associated Smelters in Port Pirie, South Australia, which has been adopted for the most recently built lead smelters. In this sintering method an ignition layer of sulphide con-

centrate is first laid on the grate and downdraft ignited; the bulk of the charge is then placed on top of the ignited layer and the blast reversed to updraft, so that the heat is carried away from the grate. In this fashion the grate is protected and any molten lead compounds are solidified by the cold blast on their way down through the charge.

In order to ensure the high mechanical strength required for sinter in a blast furnace it is usual to dilute high grade lead sulphide concentrates charged to the sinter machine, due to the low melting point of PbS. Rich lead sulphide concentrates, containing say 55 to 75 % Pb, are therefore usually downgraded with limestone and silica to give sinters with 35 to 40 % Pb. This is obviously not economically attractive since it increases the blast furnace burden and hence coke consumption, and because it increases lead slag loss because of the greater slag volume produced. To overcome this problem the Boliden Mining Company in Sweden developed some years ago a method for producing high grade lead sinter by charging to the sinter machine balls with successive layers of recycled sinter material, fluxes and sulphide concentrates; these composite balls were built up in successive pelletizing drums. In this way it was possible to produce a sinter with high Pb content from rich sulphide concentrates. However, Boliden have since developed a method for direct smelting to high grade lead sulphide concentrate and have therefore abandoned this sintering method.

## Continuous blast furnace tapping

American Smelting & Refining Company (Asarco) have recently developed at their East Helena, Montana smelter, a continuous tapping method for lead blast furnaces which reduces labour requirements and improves blast furnace

efficiency by ensuring continuously uniform smelting conditions. The flow of slag and lead bullion continuously tapped from the furnace is controlled by placing a box-shaped trap with an adjustable weir around the taphole.

## Lead blast furnace smelting with oxygen enrichment

American Smelting & Refining Company (Asarco) made a full scale test of oxygen enrichment of blast furnace air at their East Helena, Montana lead smelter in 1962 and similar test results were reported in 1959 from the Ust-Kamenogorsk Lead-Zinc Combine in the Soviet Union. Oxygen enrichment gave a substantial increase in smelting rate and a considerable decrease in coke consumption.

## Direct smelting of lead concentrates

St. Joseph Lead Company have recently investigated the direct smelting of lead concentrates in a pilot plant at Herculaneum, Missouri. The process consists of blowing concentrates beneath the surface of a molten lead bath by means of a stream of air. The reaction vessel is designed like a side-blown converter. The desired reaction:

$$PbS + O_2 \longrightarrow Pb + SO_2$$
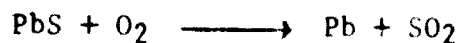
proceeds at a high rate and a high degree of completeness. The main problem has been how to keep a refractory lining in the tuyere area, and more work remains to be done on finding the best way to dispose of the slag forming constituents in the concentrates. It is therefore still too early to judge the probability of this process being developed into a reliable and economical lead smelting method.

## Direct smelting of lead sulphide concentrates

In Boliden's new smelting method dried high grade lead sulphide

concentrate, mixed with fluxes and a small amount of coke breeze, is flash smelted in vertical air jets down into an electric furnace. Most of the sulphur is oxidized before the concentrate reaches the slag surface in the furnace. The equilibrium diagrams show that at 1150° C and an $SO_2$ content of 10 % in the gas phase, the reaction of PbS with a stoechiometric amount of air should produce only metallic lead and $SO_2$ gas. In practice some oxidized lead compounds are formed and the inclusion of a small amount of carbonaceous reductant in the charge is therefore needed to complete the reduction to metal and limit the Pb content of the slag. This smelting method has now been successfully operated at Rönnskär in Northern Sweden since 1963 at a rate of 40,000 to 50,000 tons of lead annually, using a 8,000 KVA furnace equipped with 3 Soderberg electrodes in line. Lead recovery is of the order of 98 %.

The Finnish company Outokumpu Oy has for a number of years used a flash smelting process for treating copper and nickel sulphide concentrates. At their research station in Pori, Finland this company has tested on a pilot plant scale the application of their flash smelting process to lead sulphide concentrates. It has been found that lead concentrates can be successfully flash smelted but the dust circulation is very high due to the high volatility of lead compounds under these smelting conditions.

## Self-fluxing lead smelting in rotary furnace

Since about 1960 Rudniki Svinca in Topilnica Mezica, Yugoslavia have used a short rotary furnace for producing approximately 60 tons per day of lead from a self-fluxing sinter charge. The sinter mix is composed of galena concentrate, return fines, flue dust and lead sulphate sludge, and the sintered product contains 78 - 83 % Pb and 4 - 5 % Zn. Sinter is

charged at one-hour intervals to the rotating furnace which is kept at
about 1000°C. Lead is formed according to the reactions:

$$PbS + 2PbO \longrightarrow 3\ Pb + SO_2$$
$$PbS + PbSO_4 \longrightarrow 2\ Pb + 2SO_2$$

If necessary, a small amount of carbonaceous reductant is also added. After
4 to 5 cycles of charging and lead tapping, the furnace contains a large
quantity of lead and zinc-bearing residues and slag. Now the "slag smelting"
i.e. the reduction of the residues is carried out by adding pelletized NaOH
and $Na_2CO_3$ and some reduction coal. The rotary furnace is fuel oil or gas
fired.

## Fire refining of lead

Fire refining continues to be the most used refining method for
lead bullion because it requires much lower investment than an electrolytic
refinery and also because operating costs are lower than for electrolytic
refining except in comparatively rare cases where high bismuth and antimony
contents result in high fire refining costs. In fire refining the most
important recent developments have been vacuum de-zincing (following de-
silverizing of molten lead bullion with metallic zinc) and continuous
decopperizing; both processes were originally developed by Broken Hill
Associated Smelters at Port Pirie, South Australia. Bismuth removal is the
most difficult and costly step in fire refining, as already mentioned and
requires expensive reagents such as calcium, magnesium and potassium in
various combinations. This type of bismuth removal process was developed
before the last war and was known as the Kroll-Betterton process and used
calcium and magnesium as reagents. More recently. a variant using magnesium
and potassium, known as the Penarroya-Jollivet process, has been developed
in France, and was used for some time at Penarroya's lead refinery at

Noyelles-Godault in France.

## Electrolytic lead refining

Electrolytic lead refining technology has remained virtually unchanged and all refineries now in operation are believed to be based on the conventional hydrofluosilicic acid electrolyte originally developed by Betts. At the San Garino plant, in Sardinia, Italy, Monteponi and Montevecchio SpA used a sulphamic acid electrolyte on a commercial scale from 1957 but reverted in 1960 to the hydrofluosilicic acid process. The main reasons for abandoning the sulphamic acid process were lower electric conductivity and the unstability of lead sulphamate.

## Lead extraction and refining by amine leaching

Some years ago Sherritt Gordon Mines Ltd. in Canada developed a lead refining method based on the solubility of lead sulphate and lead oxide in organic amines, in particular ethylene diamine (EDA) and diethylene triamine (DETA). The proposed process comprised the following steps:

(1) acid pressure oxidation in aqueous solution to convert PbS to $PbSO_4$

(2) leaching the $PbSO_4$ and PbO in aqueous solutions of alkylene amines at room temperature to form soluble Pb-amine complexes

(3) carbonation of the Pb-amine complex solutions at room temperature by adding $CO_2$ to precipitate pure basic lead carbonate

(4) reduction of the basic lead carbonate at a suitable temperature with carbon or another reducing agent to produce $CO_2$ and high purity Pb

(5) **regeneration** of the amine leach solution with CaO at room
temperature, the $CaSO_4.2H_2O$ being discarded.

The process tested on pilot plant scale by the Bunker Hill Company
in the United States and by the Dowa Mining Company in Japan for the treat-
ment of complex Pb-Zn-Cu concentrates and residues, but has apparently been
abandoned by both companies because of technical problems and high costs

## ZINC ROASTING

Already before the last war there was a trend from hearth roasters to
other roaster designs giving higher unit throughput, richer $SO_2$ gas for
sulphuric acid recovery, and lower residual sulphur content in calcine.
The first intensive roaster for zinc sulphide concentrates, known as flash
roaster, was developed by Cominco in Trail, Canada. This design was widely
adopted all over the world between 1930 and 1960 for all pyrometallurgical
zinc processes as well as electrolytic zinc plants.

Subsequently the fluid column roaster, in which a pelletized charge
descends through a vertical shaft countercurrently to the roasting air was
developed by New Jersey Zinc Company for use in connection with their
vertical retort process. Roasting of a horizontal bed of pelletized con-
centrate was adopted by Overpelt in Belgium in connection with horizontal
retorting and by Cerro de Pasco at La Oroya, Peru in connection with the
electrolytic process. In all these cases the pelletized calcine must sub-
sequently be ground before blending into the retort charge, or to give a
large leaching surface in case of the electrolytic process.

The cost of first agglomerating the concentrate by pelletizing and
subsequently grinding the calcine pellets was avoided by the subsequent

development of a fluid bed roasting technique suitable for direct charging of zinc concentrates to the roaster. This was developed by the Vieille Montagne Company in Balen, Belgium, using a BASF fluid bed roaster, modified to meet the special requirements for zinc concentrates. In the last few years a number of Balen-type fluid bed roasters have been installed around the world, with capacities up to about 400 tons per day of zinc concentrate, and 600 tons per day units are in the planning stage. In several cases it has been possible to compare the performances of the fluid bed roasters with that of the flash roasters and it has been found that fluid bed roasting increases zinc solubility in the electrolytic process and that it is possible to obtain calcine with low sulphide sulphur content; however, the sulphate sulphur content is higher and this can be a disadvantage in those cases where there exist no natural $SO_4$ outlets, such as lead or calcium sulphate in the leach residue, from the electrolytic circuit.

## THERMAL ZINC PROCESSES

Recent developments in the conventional thermal zinc processes, i.e. horizontal retorting, vertical retorting and electrothermic smelting, are briefly discussed below.

## Horizontal retort process

This is the latest zinc process, which is a batch distillation process using small retorts with individual condensers, arranged in batteries of usually 144 retorts. At the end of world war II a large proportion of the world's zinc output was still being produced by this old process but increasing living standards gradually made horizontal retorting uneconomical in industrially advanced countries, due to the in-

creasing cost of labour and the difficulty of getting men to work under un-comfortable conditions prevailing around the horizontal retort furnaces.

The most uncomfortable and labour demanding operations, such as retort charging and residue removal, were mechanized, and zinc metal con-densation was greatly improved by the introduction of condensing systems serving jointly a large number of retorts.  Leading in these developments were Monteponi in Italy, National Zinc Company in the United States, and Vieille Montagne and Overpelt in Belgium, the latter company having developed the so-called curtain condenser.

It is however the writer's opinion that these developments can only be looked upon as prolonging the life of a process doomed by present economic trends to gradual extinction.

## Vertical retort process

Since first developing this process in the 1930's New Jersey Zinc Company have continuously worked on its improvement.  The capacity of an individual retort has gradually been increased from the initial throughput of about 4 tons of zinc per day to a present peak output of close to 10 tons per day; this has been achieved by both widening and lengthening the vertical retorts as well as better charge control, more uniform heating, etc.  Other improvements introduced by New Jersey Zinc Company are the autogenous coker, in which the volatile matter released during coking of the briquettes is used as fuel for the coking process, and the splash or dynamic condenser in which the retort gas is forced through a shower of molten zinc maintained by a graphite impeller in the condensed zinc bath.

## Electrothermic processes

Since starting up the initial electrothermic processes in Joseph-

town, Pennsylvania, St. Joseph Lead Company have gradually increased furnace throughput from initially about 25 tons per day to a present range of 50 to 80 tons per day. This has been achieved by increasing the diameter of the furnaces and particularly by increasing the power load from an initial 2500 KW to a present rating of 5,500 to 7,500 KW. At the same time, charge control has been improved so as to reduce the formation of accretions and other phenomena impeding the smooth working of the furnace. Overall zinc recovery has also been substantially improved in recent years, mainly through changes made in the residue treatment flowsheet, and is now probably the highest of any thermal zinc process.

In the early post-war years New Jersey Zinc Company developed a different electrothermic zinc smelting and distillation furnace known as the Sterling process and a pilot furnace gave promising results at Palmerton, Pennsylvania. Subsequently two full size Sterling furnaces were installed at Cerro de Pasco's La Oroya smelter in Peru but the hopes of successful commercial exploitation of this process were foiled when it was found that the reaction zone was concentrated around the electrodes so that full advantage could not be taken of the larger cross-section of the commercial furnace, and also because condensation of the distilled zinc proved difficult at the low atmospheric pressure prevailing at this high altitude in the Andes mountains. Since then, no further attempt has been made to use the Sterling process on a commercial scale.

It is interesting to note that Duisburger Kupferhütte in Germany are successfully operating a 9,000 KW furnace of a design much similar to that of the Sterling furnace. In this case, however, the charge is a high grade calcined zinc oxide with about 70 % Zn obtained as byproduct from the processing of impure pyrite cinders.

## Horizons process

Horizons Research Laboratory in the United States have developed a direct zinc reduction process. Zinc oxide in the form of calcine is suspended in a molten bath of sodium chloride. Carbon monoxide gas is sparged through the bath in the form of very small bubbles. Electrodes, located in the bottom of the furnace, maintain the bath at slightly above 1000° C. The ZnO reduced by CO gas to zinc metal vapour is carried out of the furnace by the effluent gases. A layer of charcoal covers the bath to react with any $CO_2$ formed and reduces it to CO. The chemical reactions are:

$$ZnO + CO \longrightarrow Zn + CO_2$$

$$CO_2 + C \longrightarrow 2CO$$

This process is believed to only have been investigated on laboratory scale and it is reasonable to expect that considerable problems will have to be overcome before it could be developed to a practical and reliable commercial process. At the present time it therefore seems doubtful that the Horizons process will achieve commercial significance in the future.

## THERMAL ZINC REFINING (REFLUXING)

Thermal zinc extraction processes produce more or less impure zinc of which an increasing proportion must be refined to meet the growing demand for high purity zinc. This is done by the separation of impurities, primarily lead and cadmium, from zinc by fractional distillation, using variants of the refluxing process originally developed by New Jersey Zinc Company in the 1930's. Variants of the refluxing process have been developed by several companies such as Amax in the United States, Preussag

in Germany and Overpelt in Belgium. Zinc refluxing, according to present practice, requires high fuel consumption and capital investment. There is therefore probably room for further improvements in the future, particularly since existing zinc refining capacity will have to be considerably expanded to satisfy the growing market for high purity zinc.

## ELECTROLYTIC ZINC PROCESSES

From its early beginnings the electrolytic process was developed in a number of alternatives, differing mainly on the following points:

Continuous vs. batch leaching, residue filtration and purification.

Current density in the electrolytic cells

Electrolyte cooling method (individual cells vs. entire electrolyte stream)

The advantages and disadvantages of these alternatives are briefly discussed below in view of the present and future importance of the electrolytic process.

### Leaching

Batch leaching has been adopted for several of the most recently built plants because it is simpler to operate and control than continuous leaching. Furthermore, a batch operation has the advantage of positive end point control, i.e. the operation can be carried on until the batch has reached the point where it is suitable for transfer to the next processing step. Batch leaching is usually carried out as a cycle in which calcine is first fully extracted with excess acid in the form of spent electrolyte returned from the cell room, followed by a so-called neutral leach during which excess calcine is added to neutralize the acid

solution and precipitate iron, arsenic and other impurities in-
itially extracted. In practice this neutralization requires an
excess of calcine resulting in some soluble zinc being lost in the
leach residue.

Continuous leaching is usually carried out as a 2-stage (acid
leach and neutral leach) counter-current operation and its main
advantage is a higher zinc extraction because the excess calcine
used in the neutral leach is subsequently extracted in the acid
leach stage. The 2-stage continuous leach requires additional
equipment because a solid/liquid separation must be inserted be-
tween the two leaching stages. Furthermore, accurate and preferably
automatic control systems, based on pH or redox potential are
required to ensure continuous optimum leaching conditions.

## Residue filtration

Batch filtration and washing of leach residue in Burt filters
is conventional practice in the Western Hemisphere. This method
fits well in with batch leaching but Burt filters are expensive
and require considerable maintenance. It is therefore probable
that the future trend will be towards continuous filtration on
vacuum, drum or leaf filters, and it is also probable that this
will be combined with continuous leaching so as to avoid inter-
mediary storage of leached pulp.

## Solution purification

Solution purification with zinc powder is still carried out
as a batch operation in most plants. Again, batch operation has
the advantage of a postive end control of the purified solution

before its transfer to the cell room. However, continuous purification has been introduced in several plants in recent years. The success of continuous purification depends to a large degree on the ability to continuously determine impurities at very low concentrations in the solution and this has been made possible by recent developments in analytical methods and equipment.

## Current density

From the viewpoint of investment and utilization of existing facilities it is advantageous to use the highest possible current density. On the other hand, high current density increases heat generation and attack on the lead anodes, resulting in lower zinc purity. In older plants the electrolytic cells are individually cooled by immersed cooling water coils and the electrolyte flow is quite slow. When increasing the current density to high levels it became necessary to remove larger quantities of heat; this has been achieved by greatly increasing the electrolyte flow and cooling it in large evaporative coolers outside the cells. This development, together with control of dissolved lead by addition of barium or strontium salts has made it possible to operate successfully at current densities up to 85 amperes per sq. ft. (915 amperes per $m^2$). In spite of these improvements it is still much easier to produce a good and thick zinc deposit at a high current efficiency when operating at a low current density and it is therefore not necessarily economically advantageous to operate at high current density. In this connection it must be remembered that the operations requiring most labour in an electrolytic zinc plant are the stripping of cathodes, and the maintenance of anodes

and cathodes. Labour requirements for these operations are reduced
when a thick zinc deposit is produced and when cathode and anode
corrosion is at a minimum, and these results are most easily
achieved at low current density.

It must here be pointed out that all these various alternatives
have been used in plants recently built and opinions vary consider-
ably amongst electrolytic zinc plant operators as to which alterna-
tives are the best. Consequently no definite trend is discernable
in electrolytic zinc processing except the previously mentioned
trends towards fluid bed roasters, and of course the general trend
towards increased mechanization, instrumentation and automation.
In connection with mechanization it should be mentioned that
electrolytic zinc people's age-old dream of mechanizing the cathode
stripping operation appears to have been finally solved in Japan.
A mechanical stripper developed there still probably requires
further testing and improvement but the basic principle appears to
have been established and one can therefore expect this labour
demanding operation to become mechanized in the future.

## Pressure leaching

Pressure leaching of zinc concentrate with elemental sulphur
recovery has recently been developed by Sherritt Gordon Mines
Limited in Canada and this process has also been investigated by
others. The zinc sulphide concentrate is leached with sulphuric
acid, in the form of recycled spent electrolyte, at elevated
temperature under controlled oxidizing conditions whereby zinc is
oxidized to soluble zinc sulphate while sulphide sulphur is only

oxidized to the elemental sulphur stage. The main advantages of the process are high zinc extraction also in the case of zinc concentrate with high iron content (since no insoluble zinc ferrite is formed as is the case in roasting), and the possibility of recovering elemental sulphur. Consequently the pressure leaching process could be of interest for future electrolytic zinc projects, particularly in cases where marmatitic zinc concentrates have to be treated and where no market exists for byproduct sulphuric acid.

Roasting is not entirely eliminated by this process since a certain amount of calcine is required to neutralize excess acid in the leach solution. Also, it should be mentioned that certain technical aspects, such as the separation of elemental sulphur from leach residue and the behaviour of various impurities, require further investigations before pressure leaching can be considered ready for commercial use.

## COMBINED LEAD-ZINC PROCESSING

It has already been explained that the lead-zinc industry must increasingly depend on complex lead-zinc ores giving lead concentrates with high zinc content and vice-versa, or even mixed lead-zinc concentrates. The combination of separate lead and zinc processes, and the use of the joint lead-zinc Imperial smelting process have therefore acquired increased importance in recent years and this trend will undoubtedly continue.

In lead smelting the zinc present in the lead concentrate reports in the lead furnace slag, from which the zinc can be recovered by the process known as slag fuming. This normally produces an impure zinc oxide which can be further processed to metallic zinc by any of the thermal processes

or the electrolytic process - usually by the latter.

In zinc processing the lead present in the zinc concentrate usually reports in the retort or leach residue, in the latter case in the form of insoluble lead sulphate. Most residue treatment processes recover this lead in the form of an impure lead oxide or sulphate which can be added to the lead smelter charge for further processing to metallic lead.

Slag fuming and zinc plant residue treatment, as well as the Imperial smelting process, are therefore discussed in other sections of this paper.

## IMPERIAL SMELTING PROCESS

This is the most recent development which has achieved wide commercial application in the lead-zinc industry. This process was developed by Imperial Smelting Corporation at its Avonmouth smelter in England. In the last few years a number of Imperial smelters have been built in various parts of the world.

The Imperial process is the only commercial process for simultaneous recovery of metallic lead and zinc from a charge containing both metals. The iron content of the charge has only a small effect on metal recoveries, in contrast to the retort and electrolytic processes where zinc recovery and maintenance costs are seriously affected by iron. The Imperial process is therefore particularly attractive when treating a mixed charge of lead and zinc concentrates, impure concentrates including those with high iron content, and lead-zinc bulk concentrates, provided coke is available at a reasonable price.

In the Imperial process the lead and zinc concentrates with fluxes are sinter-roasted on a Dwight-Lloyd type sintering machine. The sinter

is reduced with preheated coke in a blast furnace of special design. The volatilised zinc is condensed in molten lead, from which the zinc separates by cooling. The lead contained in the charge is recovered from the bottom of the blast furnace in the form of molten lead bullion.

The zinc metal is quite impure, due to a high lead content originating from the condensing method. Refining of the metal is therefore required for all grades other than the most lead-rich type of G.O.B. (Prime Western) metal. The lead bullion contains the silver and gold present in both lead and zinc concentrates, as well as the usual impurities in blast furnace lead bullion. It is therefore necessary to refine the lead and at the same time recover the valuable byproducts collected by the lead bullion.

The Imperial smelting process is described in greater detail in other papers presented at this meeting but new technical developments should nevertheless be mentioned within the framework of this paper. The most important recent potential developments are therefore briefly described below.

## Single condenser

The original Imperial furnace design had two condensers, one on each side of the shaft. Recent furnaces have been equipped with a single large condenser, and this simplifies the gas handling system and lowers the overall capital cost of the furnace installation. The single condenser has now become standard.

## Increased blower capacity

The production capacity of the Imperial furnace is a function of its carbon burning rate. It has been found that this can be increased by

increasing the blower capacity, and it is possible that the furnace capacity can be further extended in the future in this way.

## Air preheat temperature

In the early days of the Imperial process the furnace air blast was preheated to about 500° C in continuous tubular air preheaters built of heat resistant steel. The air temperature was gradually raised and is currently 650 - 700° C in most plants equipped with this type of air pre-heater. Recently built Imperial plants and those now under construction are being equipped with refractory bricked Cowper stoves designed for air preheat temperatures of 850° C and possibly higher. As the Cowper stove air preheat temperature is gradually pushed up, this is expected to further increase the zinc output per furnace day and per ton of coke.

## Oxygen enrichment

Preliminary tests with oxygen-enriched furnace blast conducted on the experimental blast furnace in Avonmouth in 1962 indicated that the carbon burning rate and hence the zinc output of the Imperial furnace might be increased by this method. In order to obtain more reliable information on this subject a number of oxygen enrichment tests were run on the standard size furnace at Swansea in 1965, the last one lasting six weeks. During this test the oxygen content of the blast was increased to 27 % by the daily addition of 67 tons of oxygen. During this time the furnace operated normally and no special difficulties developed. The following table shows the increase in carbon burning rate (hot coke burned) and slab zinc output as a function of oxygen enrichment:

|  | 21 (air) | % Oxygen in blast | | | |
|---|---|---|---|---|---|
|  |  | 25 | 27 | 30 | 32 |
| Carbon burning rate | 100 % | 119 % | 129 % | 143 % | 152 % |
| Zinc output | 100 % | 120 % | 130 % | 144 % | 154 % |

Further test work is required in this field but it is reasonable to expect that oxygen enrichment could improve the economy of the Imperial smelting process in locations where the power cost is sufficiently cheap for low cost tonnage oxygen production.

## Campaign life

The Imperial furnace campaign duration is an important economic factor because of the lost production and the cost of cleaning out the furnace and auxiliary equipment between campaigns. The periodical shut-downs are caused by accretions which lower the furnace efficiency. Up to 1962 the campaigns rarely exceeded 3 months but through improved process control it is now possible to figure with much longer campaigns - up to 18 months or even more.

## Larger unit size

Until 1969 all Imperial smelter projects were based on the standard size Imperial furnace, which has a shaft cross-section of 185 sq. ft. However, in December 1967 Imperial Smelting Corporation commissioned a considerably larger furnace at the Avonmouth plant. It has a cross-section of 292 sq. ft. and will have a capacity conservatively estimated at 100,000 tons of zinc and 50,000 tons of lead per year. Due to starting-up difficulties and other problems it is not believed that this furnace has yet reached this production level.

## Computer control

The large new furnace (No. 4 I.S.F.) at Avonmouth has been equipped with an instrument system capable of direct digital control (DDC). This control is a recent and advanced automation technique in which a computer replaces the conventional controllers. In addition to carrying out the DDC and sequencing functions, the computer will perform an alarm-scanning routine and a data-logging role. The next step will be computerized process control to optimize both the sintering and smelting operations. Optimization of profitability is one of the main aims of the new control system; other plans include control of blast distribution to the furnace tuyeres and control of gas temperature at the top of the furnace charge. It is felt that these functions will enable the smelting conditions in the shaft to approach an ideal state.

The computer control system installed for the new Avonmouth plant is quite complicated and it will probably still take some time before the operation can fully benefit from it.

## Vacuum dezincing

The zinc produced by the Imperial furnace contains about 1.2 % Pb and this grade is too low for most applications today, and the situation will worsen as the trend towards purer metals will undoubtedly persist in the future. It is possible to obtain high purity zinc by refining in refluxing columns but refluxing adds significantly to the zinc production cost and there are obvious attractions in a simpler, cheaper treatment which could yield an intermediate grade metal suitable for the electrolytic galvanizing and brass markets.

In the search for an alternative method of purification, Imperial Smelting Processes Ltd. have developed a process based on continuous vacuum dezincing of the stream of hot zincy lead emerging from the Imperial furnace condenser. A 1½ ton per hour pilot unit gave good results at Avonmouth some years ago. A full-scale unit was then installed on one of the Swansea furnace condensers and began production of high grade zinc in April, 1967. Operating at a rate of 3.25 - 3.5 long tons per hour the unit is currently producing VDZ (for vacuum dezincing) metal of the following quality:

Pb      0.03 %

Fe      0.003 %

The Cd content depends on the cadmium content of the raw materials smelted since cadmium is volatilized with the zinc. In order to produce cadmium-free zinc it is therefore necessary to further refine the VDZ (vacuum dezincing) metal by passing it through a decadmiumizing column similar to that used in the New Jersey Zinc Company refluxing process.

Although vacuum dezincing has now been proven in a large unit, several factors still need further investigation in order to obtain a reliable technical and economic picture of the process. In particular, it will take some time to develop markets for VDZ metal, since its quality is different from the established grades.

## RECOVERY OF ZINC FROM SLAGS AND RESIDUES BY VOLATILIZATION

Lead blast furnace slags contain up to 19 % Zn, retort residues up to 15 % Zn and leach residues from electrolytic plants up to 28 % Zn. Methods based on the high volatility of zinc at elevated temperatures have been developed for recovering the zinc, and incidentally also the

lead from such materials. Unfortunately, it is difficult in practice to
recover metallic zinc due to the ease with which the zinc vapour reoxidizes
as soon as liberated. The product is therefore a fine zinc oxide fume which
is recovered by filtering of the gas. This fume contains, also as oxides,
the lead and cadmium in the charge.

It should be mentioned that St. Joseph Lead Co. in the United
States have succeeded in recovering metallic zinc from molten slag in an
electrothermic unit at their Herculaneum, Missouri smelter. This is a great
technological achievement but the difficulties and costs were so great that
the process has been abandoned, at least for the time being. A similar
process is however now commercially used in Japan on a small scale.

## Slag fuming

The slag fuming process was originally developed by the
Anaconda Company at their East Helena, Montana smelter. In this
process a coal-air mixture is blown into a molten slag bath con-
tained in a completely water-jacketed vessel. The coal:air ratio
is regulated so as to burn a substantial proportion of the coal
to carbon monoxide, which reduces zinc oxide and silicate in the
slag to metallic zinc vapour. At the same time, combustion of the
coal provides the heat required to maintain the slag bath in a
fluid state. On reaching the slag surface, the zinc vapour is
immediately oxidized to zinc oxide which is carried away with the
combustion gases. The conbustion gases are cooled, usually by
passing through a waste heat boiler, and the zinc oxide fume is
then recovered from the cooled gas in a baghouse. The collected
zinc oxide fume is a very light powder which must be densified,

so as to reduce its bulk, if it is shipped elsewhere for further processing. Densification is achieved by heating the primary fume with a small amount of coke fines in a kiln. This treatment removes at the same time most of the lead and volatile impurities, which is beneficial for further processing of the fume.

The slag fuming process is quite flexible with respect to coal quality, and sub-bituminous coal has been used successfully at the Trail smelter in British Columbia, Canada. It may also be possible to use fuel oil instead of coal.

A number of slag fuming plants are now in operation. Most of these are in North America (Canada, Mexico and the United States). Slag fuming plants incorporating new design features have recently been built by the Boliden Mining Company in Sweden, and by Broken Hill Associated Smelters in Australia.

## The Waelz process

The Waelz process was developed to extract zinc from solid materials such as calamine ores, residues and cold slag, which are not suitable for direct utilization in the conventional zinc processes. In this process the zinciferous materials are mixed with fine coke or coal and heated in a rotary kiln. The zinc is reduced and immediately reoxidized to zinc oxide fume which is recovered from the combustion gases in the same way as already described in connection with slag fuming.

Since the raw materials are cold in this case, it is desirable to carry out the reduction at the lowest possible temperature in order to save fuel, and the process is usually carried out below

the melting point.

The Waelz process has been used extensively for recovering
zinc values from residues with high zinc content. Several Waelz
plants have been shut down in recent years because improved zinc
metallurgy resulted in less zinc-rich residues being available for
Waelz treatment. However, there are still several Waelz plants
in operation in North American, Japan, Poland and Germany. In
one of the North American Waelz plants the process has recently
been modified to use bituminous coal and at the same time sub-
stantially improve zinc recovery and product purity.

## Blast furnace fuming

For a number of years the Vieille-Montagne Company in Belgium
has been treating old slag dumps containing about 15 % Zn in a
blast furnace where the crushed slag is reduced with coke and the
zinc recovered as a zinc oxide fume. The process is still in use
at the Balen smelter but several changes have been made in recent
years to reduce the coke consumption. Oxygen enriched air is now
used, and a proportion of the coke has been replaced with coal which
is mixed with residues and shaped into briquettes before being
charged to the blast furnace.

## The rapid reaction process

In recent years a process based on the flash smelting of
ground slag mixed with fine coke has been invented by Lange and
Barthel in Freiberg, East Germany, and is being further developed
by Lurgi in Frankfurt, West Germany. A considerable amount of
fuel oil or gas is also needed to provide the necessary heat for

volatilization of zinc and lead. The gases leave the reactor at a considerably higher temperature than in the Waelz process, so that waste heat recovery in the form of steam or electric power becomes feasible in this case.

The process has been investigated on a pilot plant scale but practical problems have presented its commercial application to date.

## Cerro's Zileret process

This process was developed by Cerro de Pasco Corporation at La Oroya, Peru during the period 1956 - 1962. A pilot plant treating 50 tons per day of electrolytic zinc plant residue was built in 1965 - 1967 and has been in operation since then.

In the Zileret process leach residue is first pelletized and a carbonaceous reductant incorporated in the pellets. These are then fed with additional reductant to a kiln where solid phase reduction takes place at about 1100° C. Zinc, lead, cadmium and indium are volatilized, recovered as an oxide fume and separated by hydrometallurgical methods. Copper and silver remain in the solid kiln product, which is still in pellet form and in which a large proportion of the iron is present in the metallic state. In Peru this sponge iron will be used for recovery of copper from mine waters by cementation, whereby the copper and silver values in the residue will be recovered incourse of the normal smelting and refining of this cement copper. This utilization of the sponge iron is particularly suited to Cerro de Pasco but it may be possible to recover the copper and silver values ir other ways

which would broaden the application potential of the process.

## HYDROMETALLURGICAL RESIDUE TREATMENT

In the conventional leaching of zinc calcine Pb, Ag, Au, In, Sn, $SiO_2$, $Al_2O_3$, CaO (as $CaSO_4$) remain insoluble in the residue. A proportion of the zinc and copper also remain as insoluble ferrites, as well as part of the cadmium. A proportion of the iron and arsenic are initially dissolved in the acid leaching stage but re-precipitated during the neutral phase of the leach and consequently also end up in the leach residue.

An electrolytic zinc plant leach residue is therefore a very complex material and it is correspondingly expensive to treat. Residue treatment is therefore only economically feasible if the recoverable values are sufficiently high; often this is not the case and many electrolytic zinc plants therefore send the leach residue to waste without further treatment.

Many leach residue treatment methods have been proposed, of which comparatively few have actually been used commercially. The choice depends mainly on residue composition and local conditions. A few of the newest methods are reviewed here.

### Acid re-leaching processes

A multitude of processes based on re-leaching with acid, have been proposed for breaking up the insoluble zinc ferrite but only processes based on sulphuric acid seem practical and economical because they yield a zinc sulphate solution which can be added to the electrolytic zinc plant circuit. The main problem is that too much iron is dissolved with the zinc, unless special precautions are taken to avoid this.

## Jarosite process

Recently the two companies, Det Norske Zinkkompani in Norway and Elektrolytic Zinc Company of Australasia in Tasmania, simultaneously but independently developed an elegant residue treatment process based on the elimination of iron from the leach solution in the form of insoluble double sulphates of trivalent iron and alkali metals such as sodium, potassium and ammonium.

In practice the residue is leached with sulphuric acid, in the form of strengthened spent electrolyte, close to the boiling point but still at atmospheric pressure. Under these conditions zinc ferrite is decomposed and both zinc and iron go largely into solution; at the same time a secondary residue, containing the lead and silver values in a concentrated form, is obtained. The acid sulphate solution, containing zinc and iron as well as copper and cadmium is neutralized with zinc oxide in the form of low-iron calcine or fume, whereupon iron is precipitated with ammonium, potassium or sodium sulphate. The jarosite precipitate is crystalline and therefore easily filtered and washed. The resulting neutral and practically iron-free zinc sulphate solution is joined with the main leach solution and further processed by normal purification and electrolysis.

It is believed that electrolytic zinc plants can reach overall zinc recoveries of 96 % or better by incorporating this residue treatment method and this development is therefore probably of considerable significance for the future of the electrolytic zinc process.

## Pressure leaching

Pressure leaching of residue with sulphuric acid solution has been proposed by various companies including American Zinc, Lead & Smelting Co. in the United States, Electrolytic Zinc Company of Australasia Ltd. in Australia, and Noranda Mines Limited and Sherritt Gordon Mines in Canada, but it is not believed that any such method has been used commercially to date. The treatment proposed consists of leaching in an autoclave at 140 - 260° C with a free acid strength of 40 - 50 gpl $H_2SO_4$. Under these conditions Zn and Fe are almost completely dissolved and the solution is subjected, still under pressure, to an oxidizing atmosphere at 140 - 260° C; it is claimed that the greater proportion of iron is then precipitated as granular basic ferric sulphate which can easily be separated from the Zn, Cu and Cd sulphate solution.

Due to the complications connected with high temperature and pressure operations it is believed that the jarosite process will in the future be adopted in preference to pressure leaching.

## SUMMARY AND CONCLUSIONS

Conventional sintering and blast furnace smelting practice is still prevalent and if large lead smelters are built in the immediate future they will probably be based on this technology, but including of course modern materials handling and control methods. Oxygen enrichment may possibly be used in future blast furnace plants, and added to existing plants to increase output and reduce coke consumption.

A modern sinter plant requires a substantial investment which is economically justifiable only for a reasonably large output. New processes

which do not require sintering, such as the Boliden, Outokumpu and St. Joseph Lead Company processes, might therefore be chosen in the future for smaller projects. Of these, only the Boliden process is fully developed at the present time.

Fire refining will undoubtedly be used for refining lead in the future, and these lead refineries will include modern features such as vacuum desincing and continuous decopperising if of sufficient capacity.

In zinc smelting the trend in recent years has favoured the electrolytic and Imperial smelting processes, as shown by the following figures giving the distribution of processes used in the world (in % of total world zinc production capacity):

| Process | 1950 % | 1968 % |
|---|---|---|
| Electrolytic | 51.0 | 59.2 |
| Imperial smelting process | 0.6 | 10.5 |
| Electrothermic | 4.1 | 5.7 |
| Vertical retorting | 10.9 | 8.6 |
| Horizontal retorting | 33.4 | 16.0 |

During the last decade the growth of the Imperial smelting process has been spectacular. From a new process only used in a couple of plants belonging to Consolidated Zinc Corporation (now Rio Tinto Zinc), the organization which developed and owned the process, the Imperial smelting process has become an accepted process in most parts of the world where lead and zinc are processed, with the notable exceptions of the United States and the Soviet Union. The Imperial smelting process will continue to grow in the immediate future as several Imperial smelters are now in the construction and planning stages.

However, the writer believes that the largest share of future zinc plant expansion will be based on the electrolytic process, particularly in developing countries. The reasons for this thinking are the following:

(1) The electrolytic process produces directly zinc of the highest purity and this is very important in view of the continuing trends towards higher purity requirements for all metals, including zinc.

(2) The electrolytic process is suitable for comparatively small productions and an electrolytic plant can be gradually expanded as required.

(3) New residue treatment processes, in particular the jarosite process, will result in the highest obtainable overall recoveries for zinc and other values in zinc concentrates.

(4) No zinc metallurgy is simple but the electrolytic process is still probably the easiest to operate well in developing countries with limited technically qualified personnel.

(5) The buildings and a large proportion of the equipment required for an electrolytic plant can usually be supplied locally in a developing country.

In contrast, the Imperial smelting process produces the lowest grade of zinc on the market, of which an increasing proportion will have to be refined in the future; several existing Imperial smelters are therefore now installing or expanding zinc refining facilities. The fact that the Imperial smelting furnace is the largest zinc production unit available can be an advantage in industrially highly developed countries with large zinc markets and access to capital for large investments, but can be a dis-

advantage in developing countries where it is usually wise to get started with a plant of more modest size. Also, the Imperial smelting process is best suited for industrially advanced countries because it is a complicated process requiring the highest level of technical supervision and sophisticated control equipment to achieve good performance. The Imperial smelting process will however probably get an important share of future zinc capacity, particularly in industrially developed countries and in cases where both lead and zinc raw materials are available in a suitable ratio. In this connection one must remember that there is still room for improvement in the Imperial smelting process and that its performance undoubtedly will be further developed in coming years.

The horizontal retort process is doomed to gradual extinction but existing vertical retort and electrothermic zinc plants appear to still be competitive. However, it is believed that little new capacity will be based on these processes, and that this new capacity will mostly be expansion of existing plants. It should here be remarked that the St. Joseph Lead Company electrothermic process has become a highly efficient zinc process with high recoveries and large units; however, it uses both coke and electric power and usually one of these energy sources is the most advantageous, the Imperial smelting process becoming a natural selection where coke is the cheapest and the electrolytic process where electric power is the cheapest. Nevertheless, there could be cases where the St. Joseph Lead Company process would be attractive, although little attention seems to have been paid to this process by outsiders.

Pressure leaching of zinc concentrates with elemental sulphur recovery offers interesting possibilities. However, the process is not

yet ready for commercial use and it would not be particularly well suited for developing countries because of the sophisticated high pressure equipment and expensive materials of construction needed.

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