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LEAD -- PROGRESS AND PROGNOSIS :

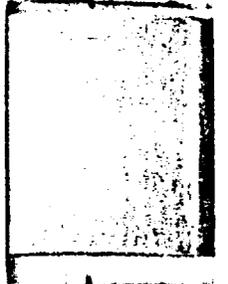
THE STATE OF THE ART : *Meeting*

LEAD RECOVERY

A. WORCESTER AND D. H. BEILSTEIN

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LEAD - PROGRESS AND PROGNOSIS  
THE STATE OF THE ART - LEAD RECOVERY

A. Worcester and D. H. Beilstein

ABSTRACT

The present methods in general use to recover lead metal from its ores, including the refining procedures necessary to produce fully refined lead metal are discussed. The major smelting and refining processes are reviewed, and include the removal and refining techniques for recovery of the major diluent metals. Possible future recovery methods, based on present and future technology, are reviewed.

A. Worcester is Assistant Blast Furnace Superintendent at the Herculaneum Smelting Division of St. Joe Minerals Corporation, and D. H. Beilstein is Chief Metallurgist and Director of Research.

Worcester/Beilstein



## INTRODUCTION

The use of lead metal pre-dates written history; the techniques for its recovery are lost in antiquity. From such early beginnings, man is now producing and recycling upwards of 4,000,000 tons annually. Lead consumption in the United States in 1970 was 1.267 million tons, distributed as:

Chemicals (including TEL)	278,000 tons
Batteries	570,000 tons
Pigments	98,000 tons
Metal (cable covering, ammunition, pipe, etc.) and Miscellaneous	<u>321,000 tons</u>
	1,267,000 tons

In this Centennial Year of the AIME, it is in order to look back at where we have been, where we are now, and where we can predict we shall be in the next decades. This, then, is the purpose of "Lead - Progress and Prognosis".

### I. HISTORICAL

Lead is one of the seven metals known to ancient man. Egyptian graves have yielded both decorative and useful artifacts of lead or its compounds. The Greeks, Thucydides and Pliny, make reference to lead, as do Homer and Cicero.

Lead deposits in Carthagina, Britain, and Scotland were mined by the Romans. Areas that are now Germany, France, and Austria have a long history of mining and lead recovery.

In the United States, the northeastern seaboard was first to be mined, and later, with the westward expansion, Missouri, the tri-state area, and the far west became the focus for lead recovery operations.

Our earliest knowledge of smelting methods is speculation, probably oxide or carbonate lead ores were smelted in the presence of carboniferous materials, in pits or hollowed logs, to produce single charges of metal. Biblical reference - Jeremiah 6:29 - indicates bellows were used for the air source. Primitive, natural wind tunnels were used in ancient Britain, and, eventually, were fabricated around a central fire.

By 1900, technology was well advanced, making use of the PbS-PbO roast reaction and reduction reactions. Refining consisted of desilverizing,

either by the Pattinson liquation process or the Parkes' zinc process, followed by oxidation of the remaining zinc and other impurities.

The roast reaction was performed in two types of vessels (in both cases, metallic lead bullion was produced, as well as a lead-bearing slag). A reverberatory furnace was used, and the charge raked on the hearth by hand or mechanical means to form Pb, PbO and PbSO<sub>4</sub>, as well as unreacted PbS. At higher temperatures, in a second step, this portion of the charge reacted with the remaining PbS to form Pb and PbO - - the PbO being a slag on the surface. The other type of vessel, an ore hearth, produced similar products, but was equipped with an air blower to hasten the reaction. This was a more continuous type of operation.

Blast furnaces were the common vehicle for smelting of the residual slags, as well as for the direct smelting of ores of low sulfur content or oxidized lead. The charges consisted of those materials, plus in-plant secondaries, with coke or charcoal as the reductant. The slag and matte production was retreated to produce a high grade material which was either smelted to black copper or to blister in the then current copper smelters.

Refining consisted primarily of oxidation of the impurities in a reverberatory type furnace. Silver was removed by either the Pattinson liquation process or, in the United States primarily, by the Parkes' process using zinc.

It is of interest that the refined lead produced by the two processes differed primarily in bismuth and copper content. Bismuth followed the rich lead and, subsequently, was removed by cupellation in the Pattinson process.

PRODUCT	LEAD	Cu	Sb	Bi	Ag	Zn
Parkes' Lead	99.98%	.001%	.006%	.005%	.0005%	.0008%
Pattinson Lead	99.97%	.015%	.01%	.0006%	.002%	.001%

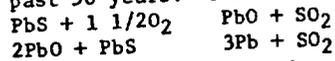
This, then, was the state of lead smelting at the turn of the century. From 1900 to the present, the technology and knowledge of the smelting and refining processes were improved to their present levels. Huntington and Heberlein developed their batch process for sintering, followed by Dwight and Lloyd's continuous process for the agglomeration of sulfide lead concentrates, with simultaneous elimination of the sulfur content. Harris developed the sodium hydroxide-sodium nitrate system for removing tin, antimony, and arsenic. Betterton improved the basic Kroll process using the Ca-Mg system for bismuth removal and recovery. Isbell developed the dezincing machine for the removal of zinc from desilvered lead. Concomittant with these technical improvements came the mechanical upgrading of equipment, and size increases of such equipment, which enabled the industry to fully utilize the processes at hand.

## II. PRESENT STATE OF THE ART

### A. SINTERING

The chemical principles of sintering have undergone no basic

changes in the past 50 years. The roast reaction of:



remains unchanged. With the advent of up-draft sintering, the need to limit the second reaction has become less important, resulting in high grade sinter. Self-fluxing sinters have become common, permitting 100% sinter charges for the blast furnaces. Sulfur elimination, utilization of the SO<sub>2</sub> gases, increased throughput, and improved product are the primary advances in the sintering operation in the past years.

#### 1. Charge Preparation

We cannot divorce the sintering process from proper charge preparation. Chemical analysis of the feed will determine what the final product analysis will be; the sizing of the total charge, the moisture content of the charge, and the degree of mixing and pelletizing all interact to produce a sinter which will react properly in the blast furnace. Three general methods of charge preparation enjoy wide use: bedding, volume controlled blending, and weight controlled blending.

- a) Bedding plants do not enjoy their former strong position, but they still are in wide use. In the bedding plant, the various materials of the charge are laid down in layers, and the total bed will provide material for from one to several days operation. Fluxes and secondary materials are added to the bed in the approximate proportions desired. When the bed is completed, it is sampled and assayed. Corrective additions are then made uniformly across the surface. At this time, the bed is reclaimed by face removal. The use of return sinter is determined by the sintering operation - - single pass sintering requires some proportion of returns, while double pass sintering, by definition, infers that all the product is sintered twice. After reclamation, the charge is mixed by mechanical means such as paddle mixers, drum mixers, mixing tables, belt transfers, or belt ploughs. The mix may be pelletized by use of a pelletizing drum or disc pelletizer before delivery to the sinter machine. In a few cases, the pellets are stored, and then repelletized on return from stock.
- b) Volume controlled blending and weight controlled blending are similar operations, in that either material volume or material weight is controlled. Both systems employ a large number of bins, each delivering a specific volume, or specific weight per unit time, of the various charge constituents. The charge consists of, but is not limited to, concentrates, fluxes, return slag, secondaries, coke,

return sinter, and miscellaneous materials.

Return sinter may be fed as a pre-set component of the charge, or as a separate individually controlled component. In the former, a change in the returns: raw ratio requires some effort, but in the latter case, a simple change in the ratio controller is needed. The bin feeders are equipped with variable feed gates. In the volume controlled system, the gate opening controls the feed rate, whereas in the weight controlled system a weigh belt will electrically demand more or less feed from the variable speed feed belt. Total feed may be varied by utilizing the jack-shaft principle, which can be a true mechanical type or an electric simile, using D. C. motors or a frequency change on A. C. motors, enabling all feed units to increase or decrease feed rates simultaneously and equally.

A typical plant would contain from 10 to 20 bins, each of up to 400 tons capacity, feeding at rates of from less than 1 ton per hour up to 100 tons per hour. Accuracy of feed is generally within 1% of the desired rate in the weight controlled circuit, with somewhat less accuracy in the volume controlled circuit.

c) Charge conditioning is a major item of any circuit. For the sinter machine to properly do its job, the charge should:

- 1) Be uniform in size - no large particles - 1/4" to 3/8" maximum size is general.
- 2) Be well mixed, to foster even sintering, with no unreacted portions in the bed, and to prevent selective air flow patterns.
- 3) Be moisture controlled, to control flame front speed of propagation, to enhance porosity of the raw and sintered bed, and to permit even sintering of the charge.
- 4) Be pelletized, to maximize production, and provide a uniform product in regard to sulfur elimination.

To provide for these conditions, hammer mills, single or multiple cage disintegrators, and crushers are used. Mixing is accomplished by mixing drums, mixing tables, paddle mixers, and other units, which also assist in proper moisturizing. Pelletizing is provided, in part, by the mixing units, and is fre-

quently enhanced by separate pelletizing drums and saucer pelletizers. The proper mixing and conditioning of the sinter charge is probably the single most important aspect of pre-sintering practice.

2. Sintering

The sinter machine proper, while basically unchanged in the last 50 years (it is still a moving grate), has become a refined, efficient piece of equipment capable of sintering 5,000 tons of material (including returns) in a single 24-hour day. Down-draft machines are gradually being phased out in the industry in favor of the up-draft principle. A comparison of down-draft vs. up-draft machines, and their operating parameters, is shown in Table I.

TABLE I.  
COMPARISON OF SINTERING MACHINE PARAMETERS

<u>PARAMETER</u>	<u>DOWN-DRAFT</u>	<u>UP-DRAFT</u>
Machine feed rate TPD	Variable (depends on 1 or 2 pass)	3,000-5,000
Available Finished Sinter TPD	200-500	1,500-2,500
Machine Size	40-72" x 50'	8-10' x 100' or more
Grate bar material	Cast iron, stainless and other hi temp. material	Cast or malleable iron
Bed depth ignition	----	1 - 1 1/2"
Bed depth burden	10"	Up to 18"
Sulfur in feed	6-10%	5-7%
Sulfur in final product	1.5 - 3.0%	1-2%
Provision for acid production	Generally no	Generally yes
Windbox pressures	-10" H <sub>2</sub> O	+20" H <sub>2</sub> O
% Pb - total	25-40	45-55
% Pb - as metallic	0-10	10-20
Speed of grate travel	Variable	40-55"/min.

a) Down-draft units are generally narrow and short, up to 60" wide and 40-50' long. General practice is

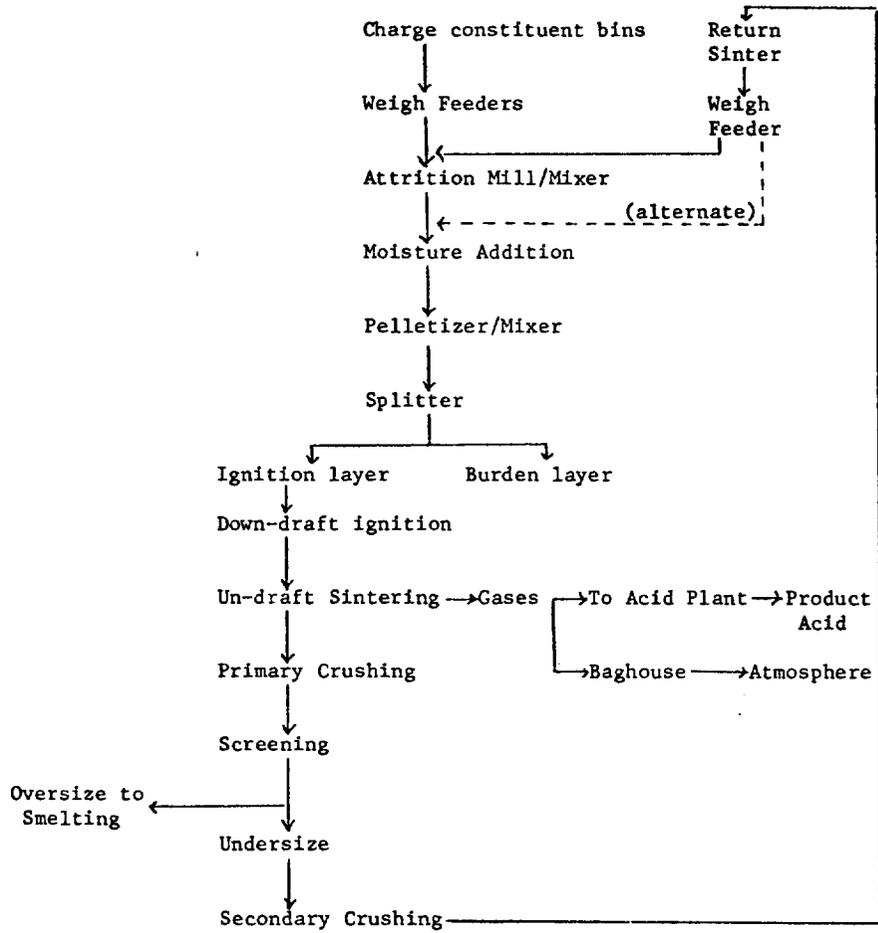
to utilize a number of machines sintering new charge, and only 1 or 2 machines to re-sinter the product. Ignition is initiated by oil or gas burners, contained in a muffle-type oven or as an open flame, evenly distributed, playing on the surface. Windboxes below the strand, under suction, draw ambient air down through the charge converting the sulfides to oxides, sulfates, and metal. The metallics drip through the charge and produce windbox lead which must be removed periodically throughout the day. Cleaning time can amount to 25% of the total available machine day, with consequent loss of production. Because of hot, dirty exhaust gases, the fans must be robust. Seals between pallet and machine are spring-loaded bars, gravity type drop bars, or a sliding seal. To utilize the SO<sub>2</sub> content of the off-gas, down-draft machines are often hooded over a portion of their length to permit recirculation of gases. This upgrades the gas to around 7% SO<sub>2</sub> by volume, which is then used for production of H<sub>2</sub>SO<sub>4</sub> in an acid plant. Without recirculation, the bed is normally open to atmosphere. After sintering, the cake is discharged, crushed, and sized for re-use or smelting. Discharge is aided by a pallet gap in the strand; the falling pallet is subject to arrest shock which loosens the cake and allows it to drop freely.

b) Up-draft sintering is becoming the accepted production method. Machines are larger, and practice is to install only one machine. The advantages of up-draft sintering are:

- 1) Production of higher lead content sinter.
- 2) Elimination of windbox lead and attendant cleaning time.
- 3) Ease of producing and collecting high grade SO<sub>2</sub> gas.
- 4) Lower sulfur in product.
- 5) Increase in usable sinter.
- 6) Lower cost of production.
- 7) Better quality of product.

Up-draft sinter machines are commonly from 8-10' wide, and up to over 100' in length. Seals between windboxes and pallets are greased sliding seals, side seal pads, or spring-loaded drop bars. The

Figure I. Sinter Plant Flow Sheet



machine is completely hooded, after the main layer feed point, to prevent gas escape to atmosphere.

Feed is divided into an ignition layer and a burden layer (about 10% and 90% respectively) by either variable flop gates, timed feed interruptors, plow arrangement, or other means. In some cases, a grate layer is provided prior to the ignition layer. The feed mechanism for the various layers may be swinging chutes, vibrating pan feeders, reciprocating belts, or drum feeders, all of which are effective.

The ignition layer (usually 1 - 1 1/2") is ignited by gas or oil in a muffle-type oven. The windbox below provides suction so that the layer is burned to the grates during travel under the muffle. The main layer is then laid down (9 - 16") and updrafting, from the pressurized windboxes, passes air upwards. The cake is burned to the surface within 20-30' of travel. No windbox lead is produced since the lead is retained in the sinter as lead globules. The remaining machine length caters for tempering and cooling of the sinter cake.

Up-draft sinter machines operate without a pallet gap at the discharge end; the weight of the sinter cake causes it to slide off the pallet at the end. After discharge, the sinter is crushed to size, and screened to remove fines and whatever percentage is needed for the proper returns ratio. It is then ready for smelting or use as returns.

High grade SO<sub>2</sub> gas is used for sulfuric acid production; barren gases are vented through a dust and fume collection system.

While there is no standard flow sheet for a sinter plant, Figure I depicts a sinter installation that encompasses general, idealized practice at present.

#### B. HEAVY SMELTING

With the present ability to produce large tonnages of good quality high grade sinter, blast furnaces have, in the last 50 years, matured to large, high throughput units. Metallurgically, charges consist entirely of self-fluxed sinter and coke. The sinter has a balanced SiO<sub>2</sub>-FeO-CaO ratio and incorporates all of the fluxes, which simplifies blast furnace charge make-up. The slags are chemically tailored to not only optimize blast furnace operation, but provide a proper charge for subsequent zinc recovery operations. Typically, slag will contain 12-18% zinc. The lead levels in a slag are low, but are not as much a concern as in the past, because zinc recovery operations also recover the lead values. It is not uncommon for a single blast furnace to smelt

1400 tons of sinter in a 24-hour day, and produce over 500 tons of bullion in the same period.

1. Conventional Furnaces

The conventional blast furnace is water-jacketed to within a few feet of the top. The upper portion is refractory lined, primarily for wear resistance. Except for the Imperial Smelting Furnace (which will be discussed separately), blast furnaces are generally operated with an open top, combustion gas being collected in a thimble-type top. The open top has gained wide preference because it saves furnace height, lessens the complication of feed arrangements, and fosters the stabilization of the smelting zone due to the charge being fed from the annular space between the furnace and the thimble. The off-takes are either on the top, sides, or ends of the thimble, depending on local preference. Furnace configuration has evolved from straight vertical sides, to a tapered section at the lower end. There is some work being done at present to return to the straight sided unit, and even to inverting the bosh producing a furnace wider at the tuyeres than at the top. The most popular designs are 5-6' wide at the tuyeres, and widen to 10' either quite abruptly (almost horizontally) just above the tuyeres, or by a gradual increase over 5-10' of the height. Furnace length is varied - - examples can be found from 15-30' long.

Tuyeres can be in a single or double row, one row above the other. The size and number of tuyeres is dependent on furnace dimensions and local practice. The second, or upper, row of tuyeres will consume from 30-50% of the total blast volume. The air blast is generally supplied by centrifugal blowers operating on ambient air. There is much experimental and development work being done on enrichment of the blast, using oxygen, oil, natural gas, powdered coal, and water as a vapor. Oxygen enrichments up to 26-27% O<sub>2</sub> have been reported, with good results in regard to smelting rates, coke reduction, fume generation, and temperature in the furnace off-takes.

The tapping of furnace products is divided into intermittent tap installations and those using an inverted siphon for continuous product withdrawal. The tapped product is settled into a lead and slag layer in a box-type settler. The slag overflows to granulation, while the lead metal is siphon-tapped. Additional second settler use is diminishing. If matte or speiss is formed in the smelting operation, it is usually catered for by a separate tapping point in the settler. Normal practice is to tap an impure bullion from the settler, and effect copper and arsenic removal in subsequent dressing operations. Bullion is transferred to the dressing section via overhead cranes or by rail on wheeled transfer ladles. Ladle

capacity varies from 8 to 20 tons.

Slag overflows the settler and is granulated by high volumes of low pressure water (usually 500-1000 gpm @ 20-35 psig pressure). The slag, from which water has been drained, is partly recirculated to the sinter plant for lead tenor and slag constituent control of the charge; the remainder goes to storage. Recent advances have enabled the slag to be used as a molten feed to a slag fuming operation in which the zinc values are recovered as zinc oxide, after removal of lead from the fume.

A comparison of present furnace parameters vs. those of the 1940 era are shown below:

<u>PARAMETER</u>	<u>PRESENT PRACTICE</u>	<u>1940 PRACTICE</u>
Height	17 - 20'	16 - 24'
Width (lower tuyeres)	5 - 6'	3 - 5 3/4'
Width (upper tuyeres)	8 - 10'	none
Length	15 - 35'	15 - 21'
No. of tuyeres/side, lower	18 - 24	12 - 28
No. of tuyeres/side, upper	18 - 24	none
Size of tuyeres, diameter	2 1/2 - 4 1/2"	2 - 5"
Air blast, volume	7-15,000 cfm	5-10,000 cfm
Air blast, pressure	25 - 50 ounces	30 - 45 ounces
Oxygen enrichment	Yes, up to 27% O <sub>2</sub>	none
Blast additive	Oil, gas, H <sub>2</sub> O, coal	none
Hearth area	75 - 180 sq.ft.	50 - 120 sq.ft.
Tons sinter smelted/day	800 - 1400 tons	300 - 600 tons
Tons sinter smelted/sq.ft. hearth	Up to 12 tons/sq. ft./day	5-10 tons/sq. ft./day
Coke burden	9 - 10%	10 - 12%
Water jacket height	16 - 19'	10 - 14'
Refractory height	0 - 5'	6 - 10'
% Pb in charge	Up to 55%	20 - 40%

## 2. Imperial Smelting Furnace

The Imperial Smelting Furnace is a specialized unit, in that it treats a combined lead-zinc sinter, and produces metallic zinc and lead. There are nine or ten of these units presently in operation or under construction. These furnaces permit economic treatment of complex lead-zinc concentrates that had been undesirable feed for either a lead or zinc smelter. Present advances have enabled the ISF to treat up to a 1:1 lead-zinc material, but more common ratios are 1:2 lead-zinc. It is also possible to treat lead-zinc sinter which contains copper up to 20% of the lead content.

Sintering practice for lead-zinc material is quite similar to that for lead charges, except that a larger proportion of returns is needed to dilute the sulfur content of the concentrates. Sulfuric acid plants are a normal ancillary to lead-zinc sinter installations.

The ISF is similar to the lead blast furnace, except that the charging system incorporates a bell and seal arrangement similar in some respects to an iron blast furnace. The air blast is pre-heated to 800°C, while the sinter charge is about 400°C as charged. Control of the CO/CO<sub>2</sub> ratio of the furnace off-gas is critical; current values are about 2:1 or better to ensure zinc vapor not being oxidized. The off-gas is collected in a condenser, atop and beside the furnace, in which circulating, molten lead dissolves the zinc vapor. This lead is constantly removed from the condensing unit and its zinc content recovered by removing the liquid, supernatant zinc layer from the cooled, liquid lead. The lower lead layer is recirculated to the condensing system where it picks up heat and, at the higher temperature, will dissolve more zinc.

The lead in the sinter charge is smelted and handled in the furnace similar to normal lead blast furnace practice, as is the slag. Subsequent handling of lead and zinc metal is similar, in most respects, to normal practice, except that the slag is a relatively zinc-free throw-away product.

## C. DROSSING

Rough lead bullion from blast furnace processes usually requires preliminary treatment before entering the refinery proper. Such treatment is referred to as drossing. The primary impurities removed are copper, nickel, and, to some extent, antimony and arsenic. Current practice is to cool the rough bullion to an intermediate temperature (700-800°F). During the cooling, copper is rejected from solution and collects on the surface as a copper dross. Depending on the sulfur, arsenic, antimony, and nickel contents, some portion of these will be carried in the dross. Fluxes such as soda ash, pyrite, and silica are added to assist

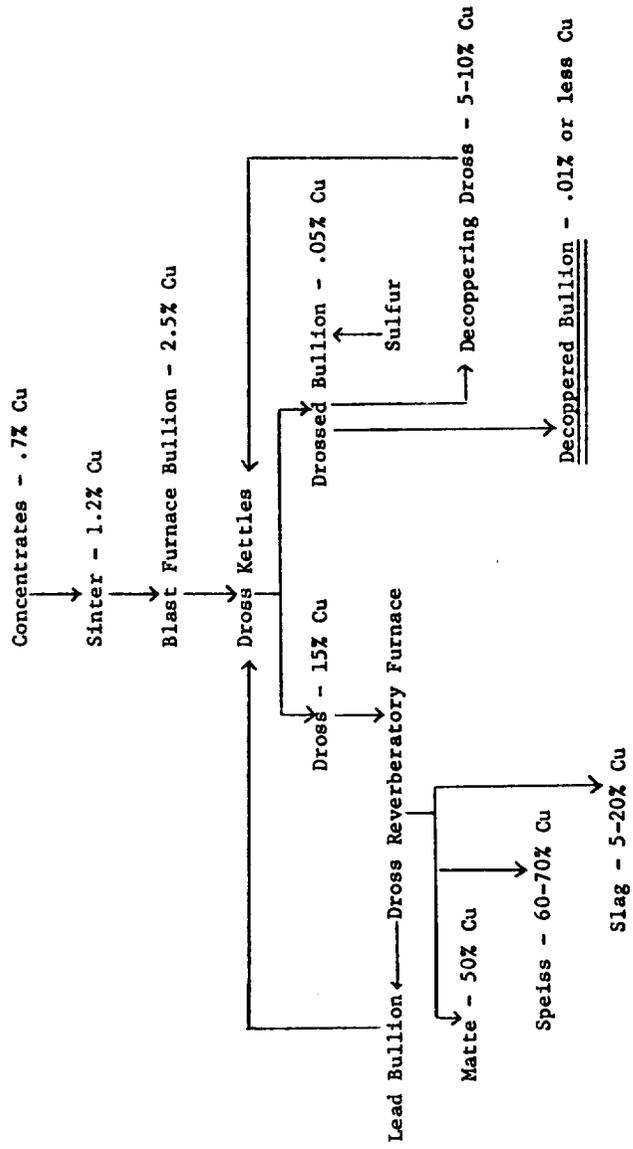


Figure II. Copper Content Flow Sheet

in further furnace recovery of these metals. The drossing operation is carried out in steel or cast iron hemispherical kettles ranging from 100-250 tons capacity. Stirring, or other means of agitation, is employed to facilitate dross formation and minimize occluded metallic lead.

The dross is treated in a reverberatory type furnace, with or without further flux additions, to produce a more concentrated product of matte and/or speiss. Normal products of the dross reverberatory are slag, speiss, matte, and metal in a layered system; slag is on top and the others in the order listed. The three upper layers may be tapped and granulated as a combined product, or as separate products. These are routed to copper smelters for eventual recovery of the copper and other values.

Drossed bullion is further treated to further remove copper before refining. The use of sulfur or sulfur-bearing material, with or without additional fluxes, and zinc and/or aluminum is normal for copper removal. These treatments will lower the copper level to .01% or less. The higher the silver, antimony, and arsenic levels of the bullion, the more effective is the copper removal. This decoppering dross is returned to the primary drossing kettles for utilization of unreacted fluxes and upgrading before charging to the dross reverberatory for smelting. A typical copper content flow sheet is shown in Figure II.

Higher copper contents of the concentrates would affect the flow sheet only in the copper content of the sinter, blast furnace bullion, and in the volume of dross, matte, and speiss.

A start has been made in the direction of continuous drossing by Port Pirie in Australia. Blast furnace bullion is received into a reverberatory type furnace, and drossed metal is removed at an equivalent rate. The principle is to mix incoming hot metal, containing approximately 1.0-1.5% copper, with cold metal of .05-.1% copper. This results in rejection of copper from the input metal as a matte. The furnace is at an elevated temperature, resulting in molten matte as a tapped final product. Lead is continually circulated from the furnace to an outside cooling loop to provide the cold mass of metal (500-600 tons per hour). Input bullion is at 900°C, with circulating bullion at 420°C, while decoppered, tapped metal is heated to 450°C and pumped away. The similarity, in reverse, to zinc collection in an ISF installation is noteworthy.

#### D. REFINING

Two basic refining procedures are in use, either pyrometallurgical or electrolytic. All refining methods consist of one variation or another of the above procedures.

##### 1. Pyrometallurgical Refining

- a) The first step in the pyrometallurgical refining of lead is removal of antimony, tin, and arsenic (cop-

per is assumed to have been removed in the dressing plant). Two general methods are in use.

- 1) The first method is referred to as furnace softening. The bullion is treated in a reverberatory type furnace, at elevated temperatures, by reaction with air (oxygen) bubbled through the bath. This oxidizes the antimony, arsenic, and tin, forming a slag or dross. The treatment may be either a batch process or a continuous one in which feed of raw bullion and removal of softened lead are simultaneous. Usual softened products will contain less than .10% antimony and/or arsenic and/or tin. The slag product is further treated by conventional smelting means to recover the metal values. The softened lead is then ready for desilverizing and degolding.
  
- 2) The second method of softening, usually referred to as the Harris Process, involves treatment with a mixture of caustic soda and sodium nitrate. This removes antimony, arsenic, and tin, as the sodium salts of their respective oxides. Due to the process involving distinct reactions, the chemistry is well known and reagent additions can be calculated exactly. Two methods are used for Harris softening. The first method utilizes a closed reactor and circulates molten lead metal through the salts within the reactor. The second method uses a standard kettle and the molten salt mixture is stirred on and into the metal. Temperature control is important for proper reaction and reaction rates. It is possible to remove the impurities as a simple mixture of all three, or as somewhat distinct portions which are enriched in each impurity. The salts, upon saturation, are removed by either skimming or tapping off as a molten product. The product is dissolved in water and filtered while hot, leaving a precipitate which is sodium antimonate. At a somewhat lower temperature (90°C approximately), sufficient lime, as CaO, is added to precipitate calcium stannate. After filtering, additional CaO is added to precipitate the arsenic as calcium arsenate. The final metal-free solutions are returned to the circuit for re-use after evaporation of the water. Supply of new NaOH to the circuit is thus minimized. The tin and antimony salts are smelted for respective recovery of the metal values,

while the calcium arsenate may be dumped or sold. Softened lead is ready for precious metal removal.

b) The next step is removal of precious metals. Present technology makes use of the Parkes' Process, zinc metal combining with gold and silver, which forms the insoluble precious metal intermetallic at operating temperatures. In this portion of the refining stage, both batch and continuous processes are available to the operator.

1) The continuous process works best when the bullion is relatively high in precious metals. The apparatus is a much elongated kettle, with a central pipe passing down into it. The upper portion of the kettle incorporates a feed well. The kettle is in four distinct, prefabricated sections, any one of which may be heated or cooled as needed (transferring heat to or from the pipe section). This allows for sectional replacement in the event of failure of a section. In operation, with a full lead kettle, the feed well is filled with molten zinc. Impure lead (Ag + Au) flows into the well and becomes saturated with zinc. As the lead moves downward, it loses heat, and the gold-zinc and silver-zinc precipitate out and rise to join the zinc bath in the well. At the bottom of the kettle, the lead is close to freezing, and enters the vertical siphon pipe. The lead rises in the pipe, picking up heat from the mass of lead in the kettle, and leaves the circuit through a siphon arrangement. Temperature control of the various four kettle sections is critical for continued, successful desilverizing. When the silver content of the zinc in the well is sufficiently high, the metal is dipped out and new zinc added to continue the process. The continuous desilverizing process is most efficient in zinc use and will produce very high grade silver skims.

2) The batch process for desilverizing utilizes a standard design kettle (up to 300 tons capacity, as are most of the newer refinery kettle installations). The metal receives the proper amount of zinc as single or multiple additions at elevated temperature (usual zinc additions are about 1-1 1/2%, and temperature is about 1000-1050°F). As the tem-

perature is lowered, the silver-zinc skins are removed in multiple skimmings at different temperature levels. Depending on the silver content of the feed and of the skins, these skimmings may be recirculated for upgrading. At the lower temperatures, the skins are silver-deficient and zinc-rich and are recirculated for efficiency of zinc usage. If gold is present, it will also report as a gold-zinc intermetallic, but it is one of the first materials to form and is removed as a separate skim. The final metal remaining will contain .1 - .2 ounces of silver per ton (.0001 - .0006%).

- c) The third step in the pyrometallurgical refining procedure is zinc removal. At its melting point, lead will contain approximately .55% zinc, which has remained in the lead following the desilverizing operation. Standard practice is to remove zinc by distillation under vacuum. This, also, may be either a "continuous" or batch process.
- 1) In the batch process, a bell is inserted into the kettle of lead, which is at 1050°F, and is evacuated to 25-50 microns. The unit is equipped with a stirring mechanism, sealed to maintain vacuum, which continually exposes a new surface of lead. The zinc is vaporized from the bath and condensed on the water-cooled underside of the bell. Bell dimensions are varied, as is geometric configuration; however, the vacuum distillation principle is unchanged. Zinc is reduced by 90% or more; common practice results in a final zinc of less than 0.10%.
  - 2) The "continuous" process utilizes a flat cover over the reactor, which is suitably sealed. Lead continuously enters the roughly kettle-shaped reactor and flows down its sides in a curtain. A vertical, cylindrical, water-cooled section of the cover is in close proximity to the curtain of lead. Zinc vapor is condensed as metal on the water-cooled cylinder. The cover is periodically lifted out to remove the zinc deposit. Final zinc levels are similar to those resulting from the batch process. The condensed zinc deposit of both dezincing methods is recirculated to the head of the desilverizing circuit. Note that the process is not entirely continuous because of the necessity to periodically dismantle

the apparatus for zinc removal.

- d) Ores containing bismuth produce metal with all of the bismuth reporting in the refinery feed metal. The Betterson process is used for bismuth removal. This process is similar to desilverizing, except that calcium and magnesium are used in place of zinc. The addition is made at 800°F as a 40% calcium-magnesium alloy, or as separate additions of calcium followed by the magnesium. After stirring and cooling to about 700°F, the calcium-magnesium-bismuth compound is removed as a skim. At just above the freezing point, the lead is removed to the next step, and has a bismuth content of less than .01% bismuth. The bismuth skims are collected, and when a sufficient volume is available, a kettle is filled with these and some lead. The melt is treated with NaOH - NaNO<sub>3</sub> to remove the calcium and magnesium. Chlorination may also be used. Further cooling, similar to desilverizing, is carried out. During this cooling process, high grade bismuth skims are removed, which are then liquated to produce a high bismuth-lead alloy. This high bismuth-lead alloy is treated electrolytically for bismuth recovery.
- e) NaOH and NaNO<sub>3</sub>, similar to the Harris Process, are used for final refining of lead for market. This removes the last traces of antimony, arsenic, tin, zinc, calcium, magnesium, and aluminum. The skims are retreated through the smelter to recover the values. Final refined lead will commonly be of 99.99 - 99.999% purity, with the major diluents being bismuth and silver. To a large extent, casting of the lead has been automated. One hundred pound pigs are usually cast on a straight line machine at a rate of 40-60 tons per hour. A one or two man casting crew, exclusive of fork lift service to remove the automatically stacked lead, is common. Large tonnage users of lead are supplied 2,000 lb. blocks which are cast (at a somewhat slower rate) on casting wheels or a permanent mold bank.

## 2. Electrolytic Refining

Electrolytic refining of lead is generally limited to areas with very low power costs and/or excessive bismuth content of the lead ores. Lead feed to an electrolytic refinery has previously been dressed to a copper content of approximately .05%. The decoppered lead is then cast into anodes. Starting sheets are prepared from refined lead. The usual electrolyte is hydrofluosilicic acid, the acid being produced locally. Current densities are of the order of 20 amperes/sq.ft., and cell voltage is about 0.5 volts. Current efficiencies are in the 95% range.

Refined lead cathodes are melted, treated with caustic and nitre as in pyrometallurgical practice, prior to casting to shape.

The anodes are recovered after 50 - 65% of their weight is lost, and the slimes are removed. The remaining anode is remelted for forming new anodes.

The anode slimes are treated for recovery of values by melting with proper flux in a small furnace. They are then reduced to metal. The metal is softened in a reverberatory type furnace to remove antimony, tin, and arsenic as a slag, which is also further treated to recover the metal values. The softened metal is cupelled to Dore<sup>1</sup> for electrolytic refining of the gold and silver. Cupel litharge, containing bismuth, is smelted to lead-bismuth alloy, which is then desilverized by the normal Parkes<sup>1</sup> Process. The resulting, silver-free, lead-bismuth alloy is electrolytically refined to bismuth metal.

#### E. ENVIRONMENTAL MATTERS

I don't believe we can minimize the impact of present attitudes with regard to pollution. This is an area of high public, governmental, and industrial interest. We would be remiss in not pointing out that the non-ferrous industry, and the lead industry, in particular, have been in the forefront of abatement equipment installation in the past, and are still revising and improving their collection systems.

Baghouses are the most common dust and fume collectors. From a small beginning in the late 1800s, the industry is presently using installations with capacities of 500,000 cu. ft. per minute or higher. The newer fabrics such as orlon, teflon, and fiberglass have enabled operating temperatures to rise to over 400°F. Bag life, in numerous instances, has reached four years. Modern baghouses have reported efficiencies of 99.8% and higher. Baghouses operate with a bare minimum of labor, often none, and are automatically cycled with respect to shaking and dust removal.

Electrostatic precipitators are not as common as baghouses, but enjoy considerable usage. They date to the period of World War I for their initial use, and enjoyed greater favor in that period. Their advantage lies in the ability to treat hot gases (as against baghouses which normally require cooling of the gas, and consequent greater volumes to be treated). Electrostatic precipitators require more rigorous pre-treatment of the gases (for electrical characteristics) to effect good efficiencies of collection. At the optimum, precipitators will approach baghouses in collection efficiencies, but more commonly are in the 95 - 98% range.

In a more recent development, generally post-World War II, it has become usual to install an acid plant to produce sulfuric acid from waste gases of the sintering process. The advent of up-draft

sintering, and resultant ease of producing and collecting high grade SO<sub>2</sub>, was one of the important factors in this development. SO<sub>2</sub> gas strengths are commonly upgraded (by recirculation or controlled sectional collection) to 4 - 7% SO<sub>2</sub> by volume. This SO<sub>2</sub>, after cleaning and conditioning, is converted to SO<sub>3</sub> and subsequently to H<sub>2</sub>SO<sub>4</sub>. In a limited number of installations a liquid SO<sub>2</sub> product is produced.

There will undoubtedly be larger, more numerous, and improved dust and gas collection systems installed in the very near future, as the demand for, and the technology to produce, an even cleaner environment increases. We shall also probably see combination systems involving cooling chambers, settling chambers, spray chambers, and other pre-filtering or pre-precipitation units improved and enlarged to enable optimum cleaning efficiency to be reached.

The dust and fume product of the collection system is recycled to the sinter circuit for value recovery. In many cases, cadmium is sufficiently high to warrant separate treatment of the dust. In this instance, the dust is leached with sulfuric acid, filtered, and the residue returned to the sinter circuit. The solution, after purification to remove lead, arsenic, and other impurities, is stripped of cadmium by precipitation with zinc metal. The sponge cadmium is refined in a kettle, or by distillation, to remove zinc, thallium, and other metals. Usual products are ball, stick, and bar cadmium. Thallium residues are re-worked to recover thallium, if economical.

### III. THE FUTURE OF LEAD RECOVERY

Future advances in lead recovery can be grouped into two general stages. The first, or near future, will see improvements in present processes; while the second, long term period, will make use of knowledge being developed today involving processes other than the common practice of 1970.

#### A. NEAR FUTURE

The preparation, and actual sintering, of the sinter charge will be optimized as we gain more complete knowledge of the effects and advantages of sizing, mixing, pelletizing, moisture content, and similar parameters. Sintering will probably be performed with some oxygen enrichment, at least in the early part of the sintering process, to provide a minimum volume of high strength SO<sub>2</sub> for acid production. Lead grade of the sinter will probably rise to a level closer to the concentrate as we are able to achieve the physical and chemical quality required of the mixed feed.

Blast furnace smelting will improve with the above optimized sinter. Oxygen enrichment of the blast will be common, as will some addition of oil, gas, water, or coal to the blast.

Furnace design will become more of a science than an art. The furnaces in various smelters will be less different from each

other. Standardization as to bosh location and dimension, tuyere size and spacing, height of column, type of charge mechanism, handling of off-gases, lead and slag tapping, and disposal (or subsequent re-treatment) will all become more prevalent as the sinter becomes better controlled.

The Imperial Smelting Furnace has led the way towards some modeling of lead smelting to iron practice. Hopefully, we shall devise means to completely seal a blast furnace, with the attendant advantages of limiting and collecting off-gases. With the tremendous improvement that iron furnaces have undergone, we are remiss in not having somehow made similar strides. Surely the advantages to be gained make the challenge and reward worthwhile.

The refining processes will be improved, most likely along the continuous lines pioneered by the Port Pirie metallurgists and engineers. The process will eventually become a truly continuous one, rather than an interrupted, semi-continuous process as at present. Engineering and metallurgy should make it possible to treat any grade of bullion in a continuous stream through drossing, softening, desilverizing, dezincing, final refining, and casting.

#### B. LONG TERM FUTURE

In this particular area, I believe we should allow ourselves to forget the past and look far into the future, bearing in mind that as the past tells us the present, the present will tell us the future. I call to your particular attention the need to nurture and protect the environment. In the future, this aspect will be of primary importance. We in the lead industry have always been the leaders in air pollution abatement, whether it be bag-houses, electrostatic precipitators, wet scrubbers, recovery of SO<sub>2</sub> as sulfuric acid, or even exotic trace element metal recovery. The lead industry has set the tone and shown the way.

We will probably see a period during which one-step pyrometallurgical procedures will see favor. Processes are already existent for this. The Worcester furnace is a prime example - - lead concentrates can be fed into the furnace and slag and bullion will be the products. Products of combustion will be greatly minimized compared to current practice. Collection will be simpler, since it will be from a single source. Similarly, the St. Joe Direct Reduction Process accepts concentrates as the feed material, and produces metal bullion and slag as the product. Combustion product handling is minimized. The U.S.B.M. long ago published its work on hydrogen reduction of the sulfide, producing metal and elemental sulfur, although, in this case, the thermodynamics are not entirely satisfactory. The possibility exists of vaporization of the sulfide, reaction in the vapor phase, and production of metal and gas for recovery as a pure or concentrated product.

In the long term view, the pyrometallurgical processes will fall by the way. Hydrometallurgy will supplant it. Work is already

well advanced.

The Sherritt-Gordon Process, using an ammonical high pressure leach, is but one example. Nominal temperature sulfating roasts, with or without additives, are already being reported in the literature. Chloridization has been with us as a process for 20 years or more. In all of these, the final product of the process is a salt or product suited to electrolysis for metal recovery.

Bacterial leaching is at present receiving consideration in the copper industry. There is reason to believe that some galena deposits were bacterially formed. Therefore, it is not unreasonable to expect that a bacterium can be found to convert sulfide to oxide, or some other form that will enable the product to be recovered electrolytically.

Direct electrolysis of concentrates is being investigated in many laboratories, and solutions to the problems will ultimately be found.

Apart from a true continuous refinery, I can see little improvement in the refining of lead. Present technology can produce metal of extreme purity (99.999 - 99.9999%) with little difficulty. Economics should be improved by a continuous process, but purity will be unaltered. Electrolytic technology already exists in those areas where metallurgy or economics make it a viable operation. Whether massive use of electrolysis comes into being or not is somewhat dependent on human attitudes. If the output per man-hour, or the cost of a man-hour show serious change, then we can expect electrolysis to become more attractive. However, I believe the continuous refinery will be the final answer at a cost level that will be entirely justified.

There are a number of processes for the recovery of lead that have been omitted from this discussion, not because of any economic or technological failing, but primarily to devote the paper to the major, large tonnage operations in the lead recovery industry.