THE SOFTENING, DESILVERING, AND REFINING OF BASE BULLION.

PART III.

The only lead refinery in Australasia at present at work is that of the Broken Hill Proprietary Company, at Port Pirie, South Australia. The following will, therefore, be mainly a description of the process as carried out at Port Pirie. These works are very complete. The products are soft lead, antimonial lead, refined silver, and refined gold. All by-products are worked up.

The refinery contains five units, each consisting of copper softening furnace, antimony softening furnace, two desilvering kettles, refining furnace, and moulding kettle; together with four liquation furnaces (not in use), two double retort furnaces, eight cupel furnaces, one reverberatory furnace for treating retort drosses, a doré parting plant, a small reverberatory furnace and cupola for treating antimonial by-products, and a power plant for supplying motive power, compressed air, circulating water, &c.

Copper Softening.

The base bullion from the smelters is fed into the reverberatory softening furnace through the two doors at the side and the one at the end, an implement called a "peel" being used for this purpose. A charge contains 35 to 40 tons, a usual one being 38 tons, giving about 31 tons of soft lead at the moulding kettle, the other seven tons being removed from the charge during the various processes of softening, desilvering, and refining. The charging takes two to three hours. The furnace is fired sufficiently to cause the charge to be slowly settling down while charging. The charge is allowed to stand at a low heat and then cooled back, and the solidified dross is skimmed off by a silghtly dished and perforated iron plate on the end of a long iron rod. The dross contains most of the copper as a copper-lead alloy of less fusibility than the rest of the bullion, together with any sulphides which may have been dissolved in the bullion, as well as any mechanically held foreign matter. The copper dross obtained is 3,000 to 6,000 lbs. per charge. The time of operation is from six to twelve hours, eight hours being the usual length. The operation is lengthened or shortened to suit

arrangements with the antimony softener. The dross varies in composition, containing—

Lead	70 to 80 per cent.
Copper	6 to 12 ,,
Silver	45 to 65oz. per ton

The following may be taken as typical of the composition:—

Lead	70.0 per cent.
Copper	8.0 ,,
Silver	58 oz.
Gold	.3 dwt.
Iron	.8 per cent.
Zinc	1.0 ,,
Sulphur	5.0 ,,
Arsenic	.5 ,,
Antimony	.7 ,,
Insoluble	2.0 ,,

The bullion from the copper softener contains*—

Copper	.125 per cent.
Arsenic	.094 ,,
Antimony	.18 ,,
Silver	70 to 80oz. per ton.
Gold	1dwt. per ton

The copper dross is sent to the smelters for treatment in a blast furnace, in which the various refinery by-products are retreated.

The skimmed lead is tapped into the antimony softener, which is at a lower level, crossing to it by means of an iron launder.

There is a tendency for accretions to grow on the side walls of the furnace at about bath level. The accretions are chipped off from time to time, and the effects of the chipping constitute the greatest wear and tear on the furnace. The lead bath is kept just about level with the top of the water jacket. The fuel used in the furnace is about 2 per cent. of the bullion.

Antimony Softening.

A reverberatory furnace is used of the same type and size as that for copper drossing, but is more strongly stayed, to resist the greater strain thrown upon it by the stronger firing. The sides in front of the water jacket soon burn back to the nose of the jacket in the space of a few days. The level of the lead is then kept down to the point of the

* Baly, Trans. Aust, Inst, *Mining Engineer*, Vol. xii.

jacket, and not over the top inclined side, as this latter requires very much extra firing on account of extra cooling action on the bath. These furnaces require repairing, principally relining around the bath level, about every three weeks. A good stream of water is required to be kept going through the jackets. If the side stays spring out, the bottom is apt to spring and lift up. The charge consists of the bullion from the copper softener, together with 50 to 80 bars of antimonial lead from the antimony dross furnace. The furnace is strongly fired for about six hours, during which the molten charge is stirred, so as to bring the antimony and other impurities to the surface to oxidise them. The furnace is cooled back, and as soon as the litharge and contained impurities have solidified they are skimmed off. The furnace is again strongly fired, stirred, and allowed to cool back, and skimmed. This operation is repeated until the litharge is of a bright yellow colour.

First skimming—1,000 to 2,000lb. (average 1,300 to 1,400lb.).

Second skimming—1,000 to 2,000lb. (average 1,400 to 1,600lb.).

Third skimming—0 to 700lb.

Generally, there are only two skimmings, in which case the second is a heavy one. The time is 12 to 16 hours, lengthened to suit convenience of desilvering kettle. The coal used in firing is equal to about 3 per cent. of the bullion.

The skimmings vary in composition.

Lead	70 to 85 per cent.
Antimony	7 to 12 „
Silver	1 to 5oz. per ton
Arsenic	.5 to 1.5 per cent.

The following may be taken as typical—

Lead	73.8 per cent.
Antimony	9.0 „
Silver	3oz. per ton
Arsenic	1.2 per cent.

The bullion contains small impurities, which do not materially affect the desilverising.

Copper	.10 to .14 per cent.
Arsenic	Nil to trace.
Antimony	.05 to .1 per cent.

The bullion is tapped into desilvering kettles, which are on a lower level. The softness of the lead bullion in the antimony softener is determined as follows:—A small ladleful of metal is taken from the furnace, and quickly poured out on the clean iron floor plates. If there is more than a minute amount of antimony present, the lead runs out more or less

in beads, and the surface is white. If the lead is soft enough to be sent to the zinc kettles the lead runs in a thin sheet, the surface of which is bluish iridescent in colour. The softened bullion is tapped from the furnace into a launder, and run into the desilvering kettles, also known as the zinc kettles.

The Treatment of Antimony Skimmings.

The skimmings from the antimony softener are treated in a small reverberatory furnace, 11ft. by 6ft. 6in. internal dimensions. The crucible is encased in an iron pan, but is not water jacketed. The furnace is known as the antimony dross furnace.

The skimmings are charged into the furnace, mixed with fine coke and coal, producing bullion and slag. The slag contains a large percentage of lead and most of the antimony, the bullion containing a low percentage of antimony. If it is attempted to clean too much lead out of the slag an increasingly larger amount of antimony is also thrown out into the bullion. The bullion is returned to the antimony softener, and the slag is further treated in a small blast furnace. A charge for the reverberatory furnace is —

Antimony skimmings	2,800lb.
Powdered coke	110lb.
Powdered coal	110lb.

Twelve charges per 24 hours are treated, and the slag is tapped once a day. It is run out and across three matte moulds to catch any metal. The slag passes out into a compound on the floor, made of fine slag and strips of wrought iron. After cooling, the slag is broken up and stacked for treatment in the antimony blast furnace, which is only run periodically.

Bullion	100 to 150 bars per day
Slag	8,000 to 13,000lb. per day

A typical analysis of antimony dross furnace slag and bullion is—

Slag—

Lead	52 per cent.
Antimony	27 „
Aresnic	5.5 „
Silica	0.7 „
Silver	2.0oz. per ton

Bullion contains—

Arsenic	Trace
Zinc	.005
Copper	.12 per cent.
Antimony	.66

The slag from the antimony dross furnace is treated in a small water jacket blast-furnace, 32in. by 48in. There are four tuyeres, each 3in. diameter. The shaft is 10ft. 6in. from tuyeres to flue. Composition of charge—

Antimony slag	450lb.
Returned slag	250lb.
Scrap iron	10lb.
Coke	90lb.

About 32 charges per eight-hour shift are treated, producing 70 to 75 bars of antimonial metal. The iron takes up most of the arsenic and some of the antimony to form a speiss. About 5 to 10 tons of basic slag is obtained from the smelter, and used over and over until it is foul, and it is then sent to the dump.

ANTIMONIAL LEAD.

Lead ...	...	76·0 per cent.
Arsenic	...	1·8 ,,
Zinc ...	...	0·1 ,,
Copper...	...	0·2 ,,
Antimony	...	21·5 ,,
Silver ...	...	2·0 ozs.

ANTIMONY BLAST FURNACE SLAG.

Lead and Antimony		6·2 p. cent.
SiO_2	... ...	30·5 ,,
FeO	... ...	26·9 ,,
MnO	... ...	3·8 ,,
CaO	... ...	9·5 ,,
Al_2O_3	... ...	17·0 ,,
Zn	... ...	5·0 ,,
Ag	... ...	1·0 ozs.

There is very little silver in the antimonial metal or blast furnace slag, most of it being removed in the bullion resulting from the operation in the antimony dross furnace.

The antimonial lead bullion is run out into a drossing-kettle. This kettle is semi-spherical, about 4ft. diameter. The top of the kettle is 2ft. above the floor. The kettle is set in brickwork, and the latter set in iron. Fire is placed under the kettle, so that the bullion may be maintained at a proper moulding temperature, which is below red heat. A tubular ring of wrought iron, 1in. thick by 3ft. diameter and 18in. deep, floats in the bath of molten metal. When bullion is tapped from the furnace it runs into the kettle between the outside of the kettle and outside of the bailing ring, and the dross collects as a mush on the outside of the ring, and is removed from time to time. The molten metal on the inside of the ring is carefully skimmed, and the metal then ladled out into moulds, and the surface carefully skimmed before it sets. The dross and skimmings are returned to the furnace.

THE DESILVERING OF SOFTENED LEAD BULLION.

The Parkes process is used for removing the silver and small amount of gold present in the bullion.

Zinc forms alloys with silver, gold, lead, and copper, which have lower specific gravities and higher melting points than metallic lead. Zinc has a greater selective power for gold and copper than for silver. It is therefore, possible, to remove by successive small applications of zinc the whole of the gold, while leaving the greater part of the silver in the bullion. The amount of gold in the bullion is small—viz., about 1dwt. If the gold-silver-lead-zinc alloy obtained by the first application of zinc is directly treated and reduced to doré, the amount of gold contained in the latter is very small. The gold-zinc alloy is, therefore, returned to several fresh pans of bullion, in order to increase the gold contents of the gold-zinc crust, and ultimately to greatly reduce the amount of doré bullion to be parted.

The charge run out from the antimony softening furnace into the zinc pans is skimmed, and 1 to 2cwt. of dross removed and returned to the furnace. This dross contains 70 to 160oz.; on an average about 85oz. of silver. The process is a complicated one, and is as follows:—

Gold Zincs.

First First-zinc.—To an untreated pan is added 250lb. of spelter, melted down, stirred in, pan cooled back, and then skimmed. The skimmings are put on one side. "First time through" = B.

Second First-zinc.—Zinc according to the gold left in the pan is added, stirred in, pan cooled back, and skimmed, and skimming put on one side. = C.

Pan is now clean of gold. This pan is now zinced for silver, in the manner described hereafter.

Another pan of bullion is then treated as follows:—

First First-zinc.—Both of the above zinc skimmings (B and C) are put together into the pan, and stirred, the pan cooled back and skimmed, and the skimmings put on one side. Known as "First zinc second time through" = A.

Second First-zinc.—Spelter or scrap zinc is now added, the amount varying according to the amount of gold left in the pan. The zinc is stirred in, pan cooled back, and skimmed. The skimmings are put on one side as a second first-zinc = C. The pan is clean of gold, and is then treated for silver.

A third pan of bullion is treated as follows:—

First First-zinc.—The previous second first (C), together with 150lb. scrap zinc or 120lb. ingot spelter, is added, stirred in, pan cooled back, and skimmed, and called "first-zinc first time through" = B.

Second First-zinc.—Then sufficient zinc to clean from gold is added, stirred in, pan cooled back, and skimmed, and the skimmings put on one side. = C.

A fourth pan of bullion is treated as follows:—

First First-zinc.—To this pan is added a first time through first skimming (B), and also second first skimming (C), stirred in, pan cooled back, and skimmed. This skimming is a "first-zinc second time through" = A.

Second first-zinc as before, product = C.

A fifth pan of bullion is treated as follows:—

Two lots of low-grade alloy, known as "first-zinc second time through" (marked A above), are added and stirred in. After the pot has been cooled back it is skimmed, and the skimming pressed in a Howard press. The product is known as "pressed gold alloy."

Treatment of Gold-Zinc Alloys.

The gold-zinc pressed alloy is allowed to accumulate for a "run." It is fed into retorts, and kept there for four hours. No zinc is recovered, as the retort furnaces are not fired enough. The dross is skimmed off from the retort charge, and the bullion dipped out into moulds. This bullion contains about 225oz. silver and 7oz. of gold per ton of bullion. It is stacked until there are about 1,600 bars—that is, sufficient for a charge in a zinc pan. It is then fed into a zinc pan, and melted down at a low temperature. When the charging is complete the temperature is raised, and the charge well stirred, without the addition of zinc. After the pan has been allowed to cool back it is skimmed, and the skimming pressed. The pressed skimming, low in gold, is treated in sweat cupels. A large amount of zinc is added to the charge in the zinc pan, and stirred in. After the pan has been cooled back it is skimmed, but not pressed. The gold-zinc alloy, now very high in gold, is sent to the retorts. The bullion from these is run down in cupels to doré bullion, as hereafter explained.

Silver Zincings.

Second Zinc.—The first lot of zinc added to remove the greater part of the silver is known as the "second zinc." Usually the zinc added to the charge is the zinc alloy skimmed from the third zinc. If there is insufficient or no "third zinc" skimmings available, it is in part or wholly replaced by scrap zinc or spelter. In the latter case about 700lb. of zinc is added. After the "second zinc" has been added it is

stirred in, the pan cooled back, the alloy skimmed off, and pressed. The pressed silver alloy is sent to the retort furnaces for treatment, as hereafter described.

Third Zinc.—About 700 to 800lb. of spelter or scrap zinc are added and stirred in. After the pan has been cooled back the alloy is skimmed off, and set aside, to be used as a "second zinc."

Fourth Zinc.—The third zincing usually leaves the pan clean—that is, .3 to .4oz. of silver per ton of bullion. If not, a small amount of zinc is added. The amount of zinc used is determined by the amount of silver left in the charge, a table based on experience having been drawn up for that purpose. The alloy is skimmed off, and set aside without pressing, and is often fed into another pan as part of the third zinc.

The time of the whole of the desilvering (including gold) operations for each pan takes about 32 hours for each charge. About 3.2 per cent. of coal is used in this operation.

Bullion from antimony softener—

Au	1.0 to 0.6dwt.
Ag	72 to 82oz
Cu	0.12 per cent.
As	Nil
Sb	0.089 per cent.

After "first first-zinc"—

Au	19grs.
Ag	70 to 80oz. per ton

After "second first-zinc"—

Au	Trace to 5grs.
Ag	68 to 75oz.

After "second zinc"—

Au	None
Ag	20 to 30oz.

After "third zinc"—

Au	None
Ag	.3 to .5oz. per ton
Zn	.56 per cent.
Cu	.00026 per cent.
Sb	.00325 per cent.

Howard stirrers are used to stir the zinc into the charge of bullion, doing away with the very hot and laborious hand-stirring. Howard presses are used to press the excess lead

out of the zinc alloy skimmings instead of liquating the zinc crust in a liquation furnace, effecting a great saving in time and also in cost.

After the pans are clean of silver, the bullion is syphoned off, and run into the refining furnaces.

Lead Refining.

The operation known as refining is undertaken to remove any residual impurities which may remain in the desilverised lead before it is run into the moulds as soft lead. In this operation the lead is refined in a reverberatory furnace, then run into large pans, in which it is allowed to cool to a convenient moulding temperature.

These reverberatories are similar in size and construction to those used in copper drossing and antimony softening, except that the depth of the bath is naturally less and the furnace is more strongly bound together than either of the preceding, on account of the long-continued strong firing. The residual of the zinc added in desilvering is removed, together with any antimony which may not have been removed during softening.

The furnace is strongly fired, and the charge stirred to bring fresh metal to the surface. The heat is let down to stiffen the skimmings, which are then swept off into slag pots. The pots are stood aside to cool somewhat, and any lead which may have been drained out of the skimmings is tapped into bars through the hole in the bottom of the pot. These bars are returned to the furnace. The skimmings are known as "lead dross." Two skimmings are taken off. Prior to removing the second, the lead is tested for softness. The bath is stirred up, and a ladleful is removed and allowed to cool, skimmed with a piece of board, then poured into a taper mould, 8in. by 2in. by 1in., and again skimmed. The presence of antimony is shown by a white spot or frosting on the surface of the bar. The presence of zinc prevents the surface of the bar showing the characteristic fernlike crystals. The surface of the bar also does not show the typical bluish white surface or the iridiscent indigo-blue tint. The latter is a good test of freedom from impurities, although the absence of such tint is not a proof of impurity. The surface of the bar should be very easily scratched with a finger nail.

The lead dross is sent for treatment to the blast furnace. Time of operation, about 16 hours. Coal used is equal in weight to 4 per cent. of bullion.

Typical composition of lead dross—

Lead	.. .. ..	85.0 per cent.
Silver	.. .. ..	0.1oz. per ton
Zinc	.. .. ..	11.0 per cent.

After the lead has been cooled back it is tapped into the moulding kettles. Accretions of zinc compound grow on the walls of the furnace, and require chipping off from time to time. As the lead dross skimmings contain an infinitesimal amount of silver (about 0.1oz.), experiments have been made to arrive at a workable process by which to work them up to soft lead without sending them to the blast furnace, where the resulting lead again becomes mixed with silver-lead bullion, and must, therefore, again go through the whole desilvering and refining process. In one case they were treated in an iron kettle, but without success, as they stuck to the side and the kettle failed. On another occasion they were put into a refining reverberatory furnace, but without success. The bottom of the furnace failed, and the lead ran out through the bottom of the pan. They could be treated successfully in a small blast furnace set apart for their use.

Moulding for Market.

The lead pans are of cast-iron, similar to the desilverising pans, of the same diameter, but not so deep. They hold about 35 tons of lead.

The lead is here again skimmed of the dross which forms on its surface, brought to the requisite temperature, which is below red heat, and then syphoned into moulds, which are arranged in a semi-circle in the moulding pit. The skimming of litharge which is removed from the pan is returned to the refining furnace. The moulds are of two sizes. The larger give large, or "China," bars, about 11 to the ton, and are destined for the China market. The smaller give "Europe" bars, about 20 to the ton, and are intended for all markets except China.

The syphon is similar to that for emptying the desilverising pots. The horizontal limb may be worked round in a semi-circle. Each mould is separate, provided with a pair of wheels at one end, and with a stump-foot and a handle at the other. Before the moulding is commenced, and at intervals during the moulding, the moulds are white-washed with lime, Two men undertake the moulding operation, one in charge of the syphon outlet running the lead into the mould and then skimming it with a convenient iron tool; the second man stamps each bar with the number of the moulding, wheeling each bar and stacking it at the side of the pit, and replacing the mould at its original place in the semi-circle for further use. Time of operation, about four hours. The refined lead is one of the softest and purest on the English market. The following analyses may be taken as typical:—

	1	2	3
Lead	—	—	99·99366 per cent.
Silver	·00171 per cent.	·00122 per cent.	·00096 „
Copper	·000324 „	·000277 „	·00026 „
Zinc	·00171 „	·000926 „	·00187 „
Antimony	·00317 „	·00297 „	·00325 „
	1 and 2 private notes.		3. Average for year.

Soft lead for the British and European market requires to be very low in silver (.2 to .3oz. per ton). The recovery of silver to this cleanness does not pay for the silver recovered, but it is necessary to come down to this, as a larger amount gives a slight yellow tint to white lead, in the manufacture of which much of the Broken Hill Proprietary Company's lead is used. Lead containing over the above amount and less than one ounce is moulded into China bars.

Retort Furnaces.

The reort furnaces contain two compartments, back to back, with two retorts in each compartment. The furnaces are fired with gas, which is generated in a small adjacent producer. The furnace is built over regenerative chambers, to heat the air used for combustion. Each compartment is fired separately, and has its own separate producer and regenerative chambers. The directions of the current of air and furnace gases are reversed every half hour by means of a butterfly valve. An ordinary clock is fitted to ring an electrical bell, so that the time of reversal is not overlooked. Gas firing enables the temperature of the furnace to be more fully regulated. The interior of the furnace is kept clean, and the retorts kept free from adhering coke, clinker, ash etc., and therefore lasts longer. Also, in cases of failure of retort, the bullion is not mixed with a lot of ashes, etc., and is easier removed.

The retorts, 3ft. 6in. high by 2ft., are made of a plumbago mixture; they are fixed in an inclined position, and last about 50 to 60 charges. Tilting furnaces enable the charge to be more readily removed, but they do not last so long, nor are they so easily and economically fired. The retorts are baled by hand. Two men look after the furnaces, and take it in turns to bale. The man doing the baling stands on a movable platform, and dips the bullion out into moulds placed on a long iron truck. The other man takes the truck of full moulds away, tips the bullion out of the moulds, stacks it for further treatment in cupel furnaces, and places another truck of empty moulds in a handy position for his mate who is baling. The latter man is protected in front from neck to knee by a thick apron made of jute bagging. The hand and arm near the retort are protected by a thick gauntlet and sleeve of the